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Tellier et al.

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(54) **METHOD FOR IMPROVING THE FUEL EFFICIENCY OF ENGINE OIL COMPOSITIONS FOR LARGE LOW AND MEDIUM SPEED GAS ENGINES BY REDUCING THE TRACTION COEFFICIENT**

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(73) Assignee: **ExxonMobile Research and Engineering Company**, Annandale, NJ (US)

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This patent is subject to a terminal disclaimer.

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C10M 107/02	(2006.01)
C10M 159/20	(2006.01)

(52) **U.S. Cl.**
USPC **508/591**; 508/460; 508/518; 508/586

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USPC 508/591
See application file for complete search history.

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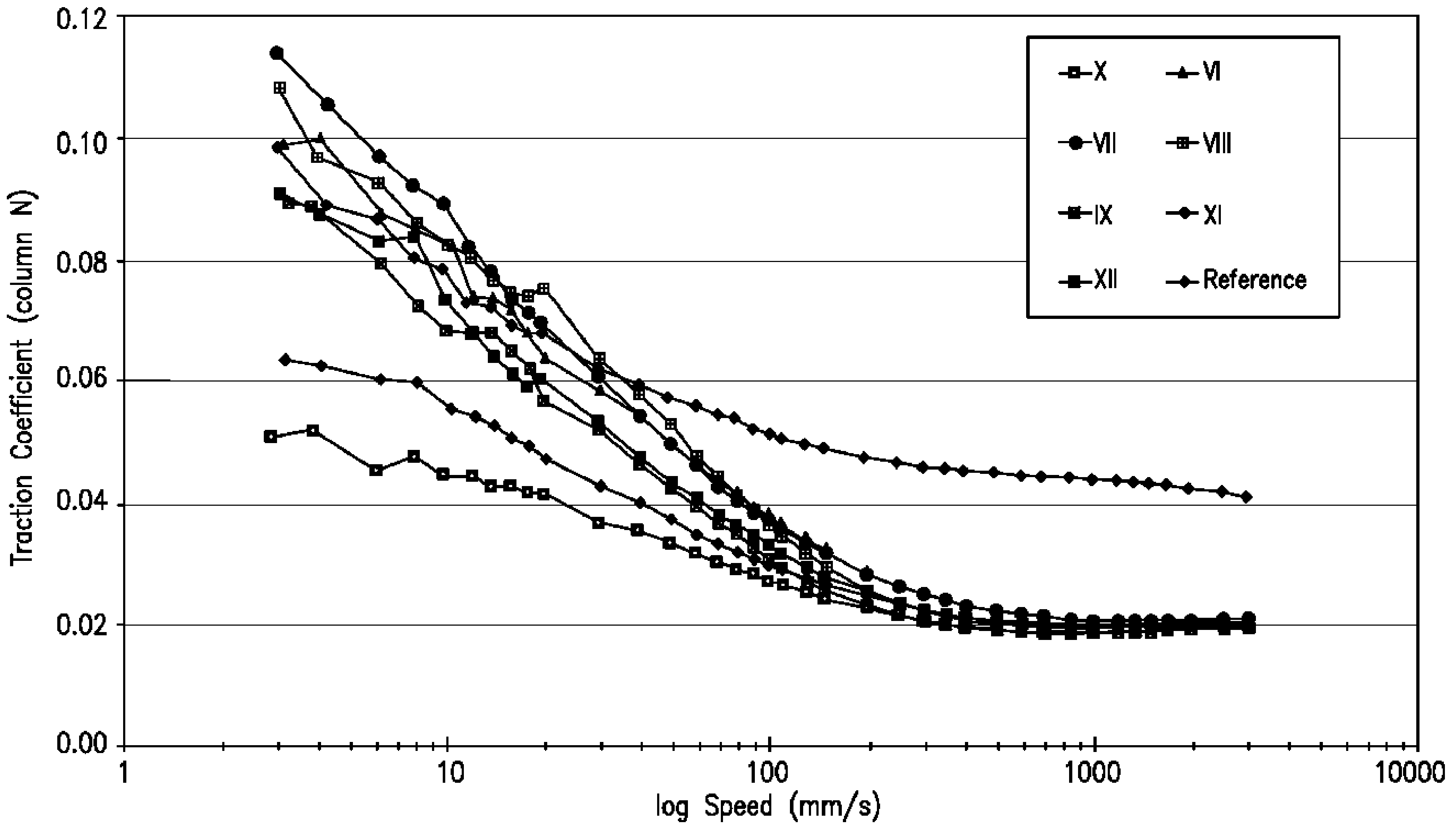
(57) **ABSTRACT**

The present invention is directed to a method for improving the fuel efficiency of large engine oil compositions by reducing the traction coefficient of the oil by formulating the oil using at least two base stocks of different kinematic viscosity wherein the differences in kinematic viscosity between the base stocks is at least 32 mm^2/s, and, preferably, additizing the composition with a salicylate detergent, a mixture of salicylate-phenate detergents or a mixture of sulfonate and phenate detergents.

6 Claims, 4 Drawing Sheets



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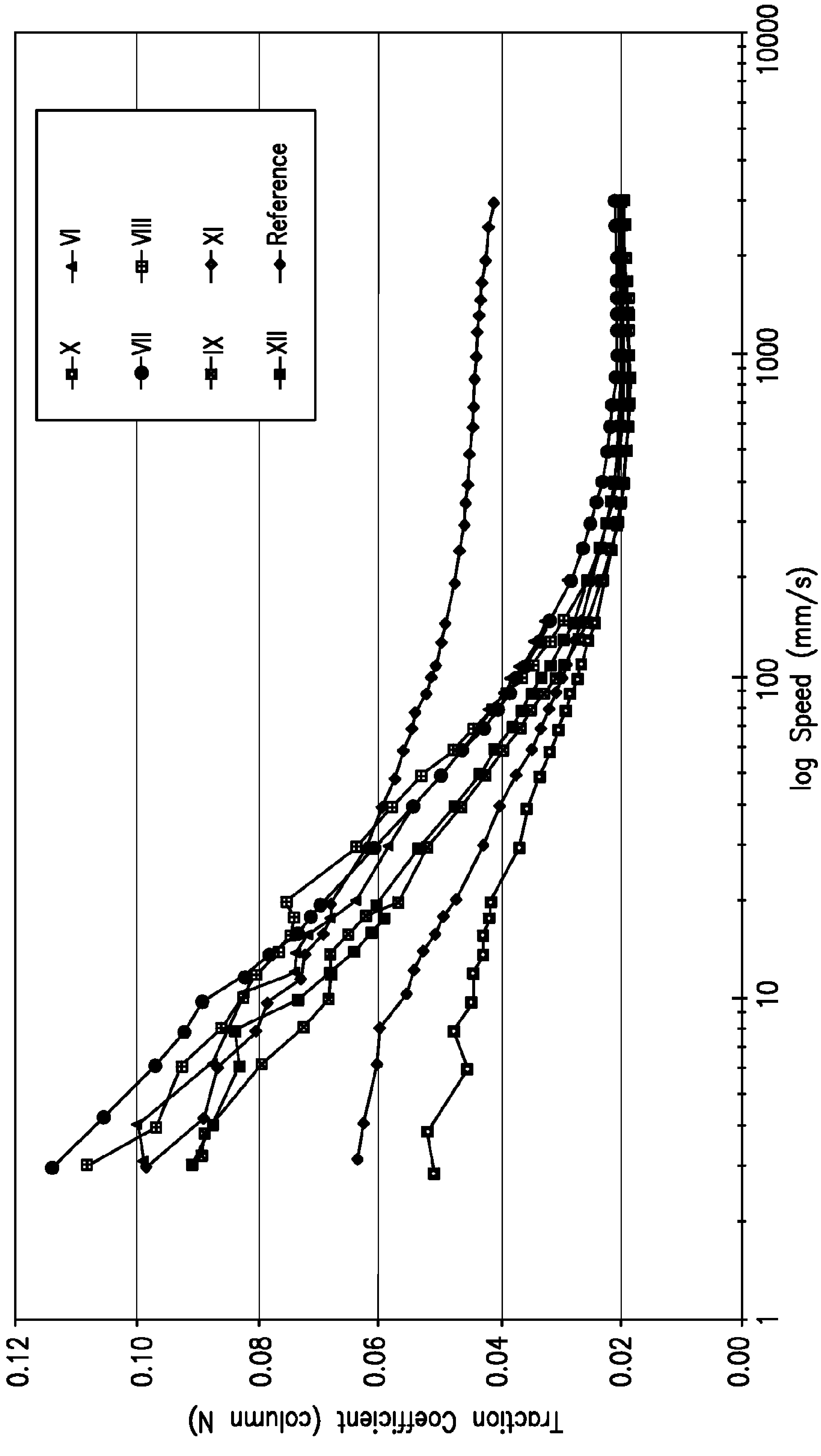
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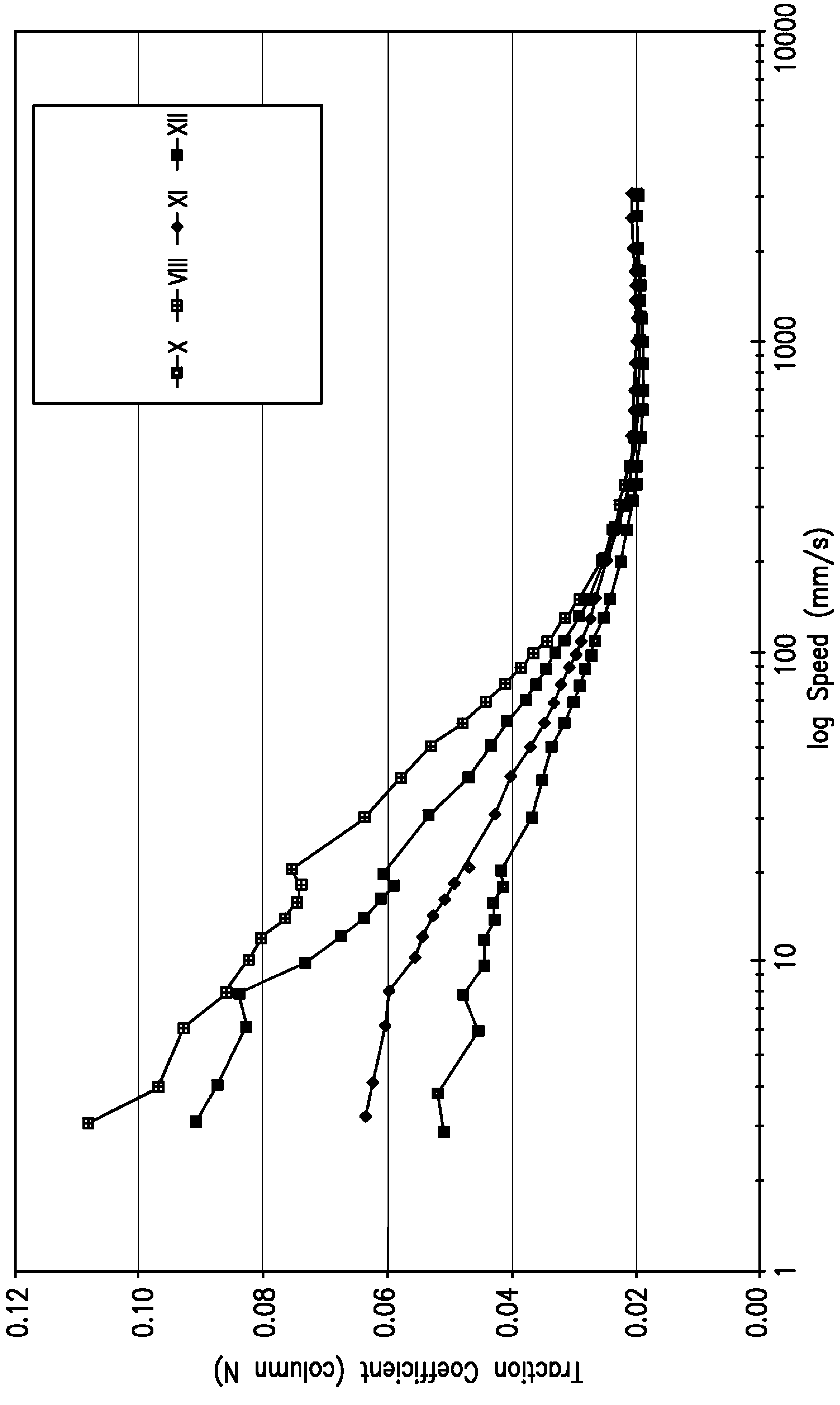
0.10
0.08
0.06
0.04
0.02
0.00
1
10
100
1000
10000
log Speed (mm/s)
X
VII
IX
XII
VI
VIII
XI
Reference

FIG. 1


Traction Coefficient (column N)
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0.04
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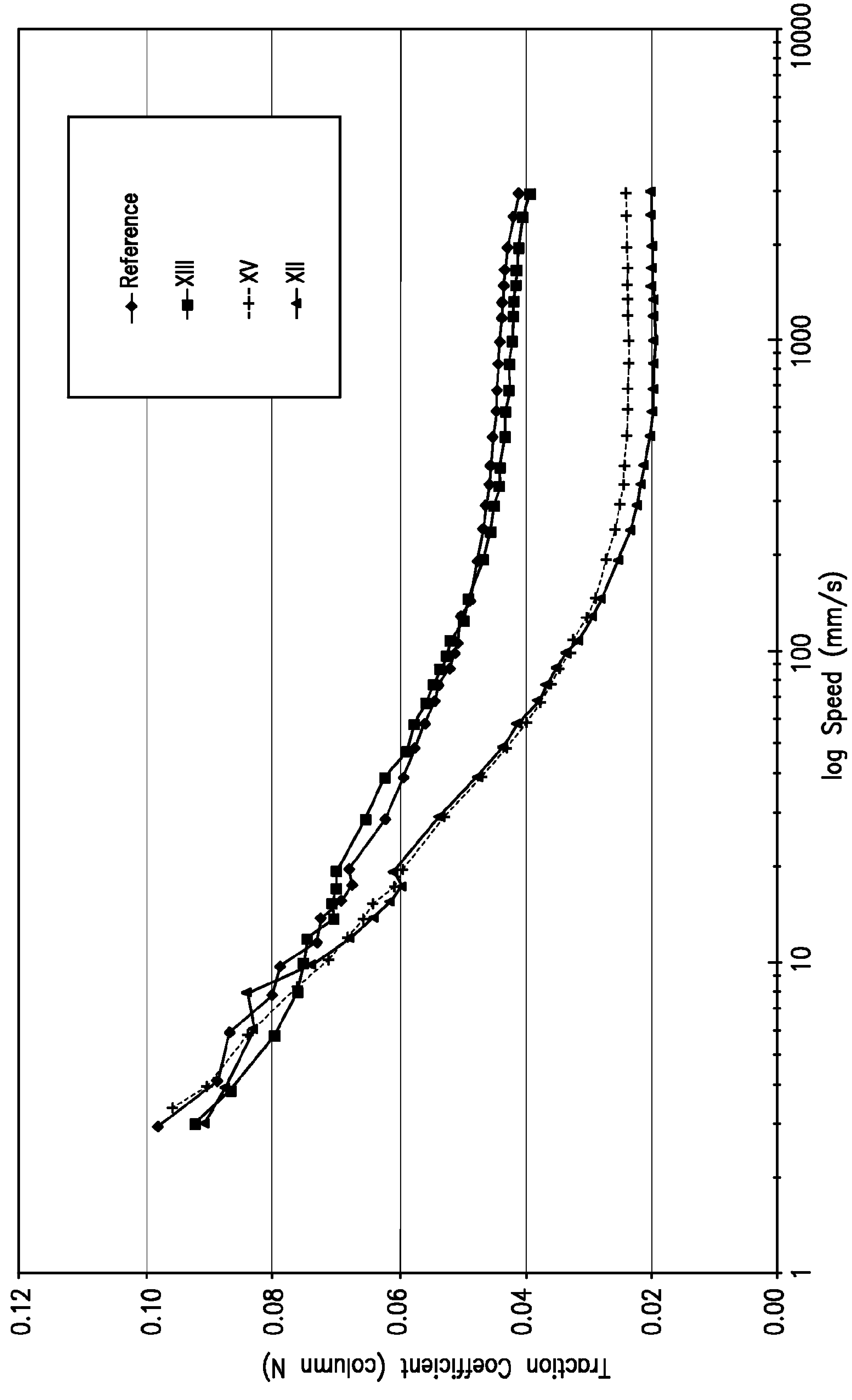
1000
10000
X
VIII
XI
XII

FIG. 2


Traction Coefficient (column N)
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0.02
0.04
0.06
0.08
0.10
0.12
log Speed (mm/s)
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10
100
1000
10000
Reference
XIII
XV
XII

FIG. 3

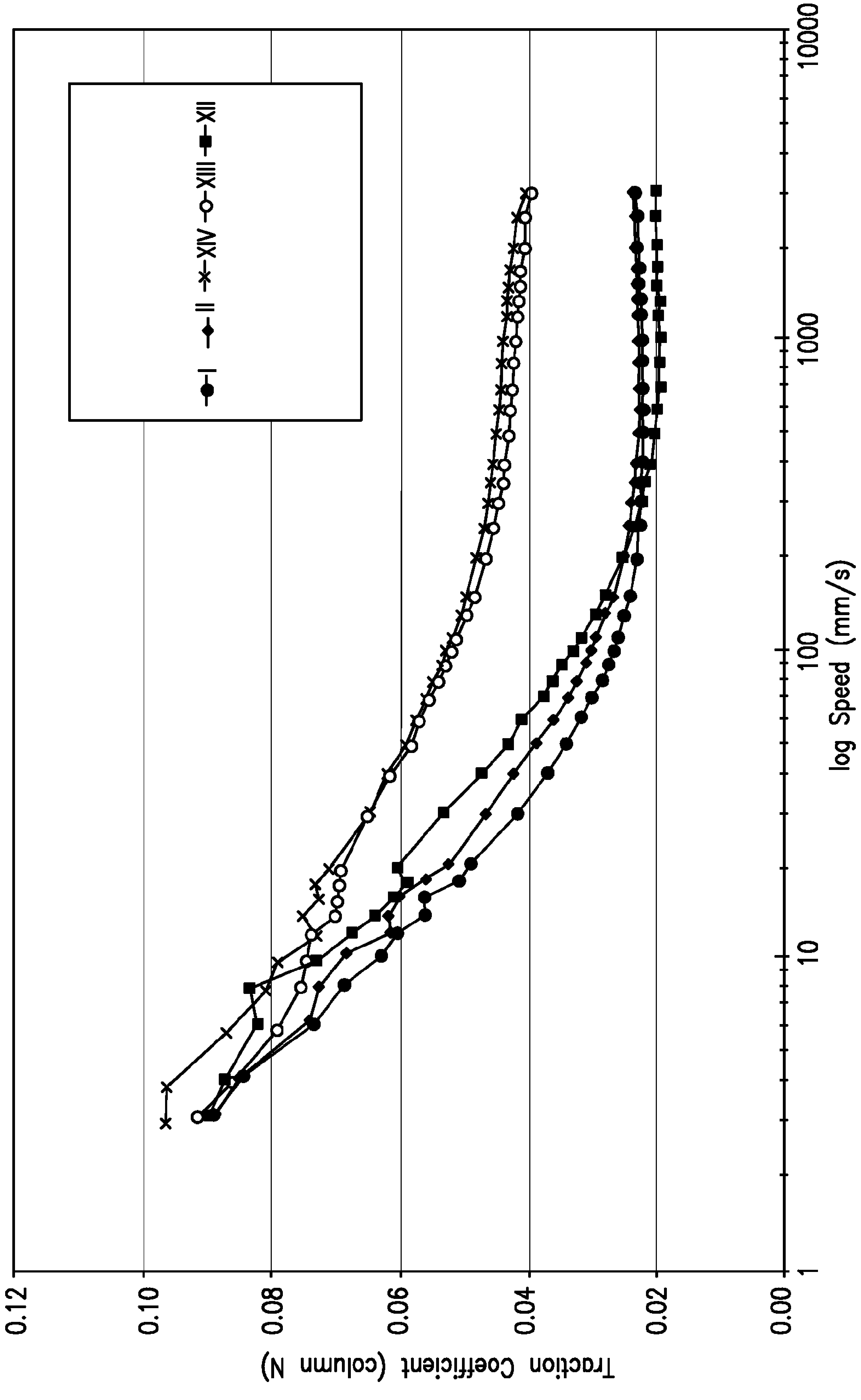

Traction Coefficient (column N)
0.00
0.02
0.04
0.06
0.08
0.10
0.12
log Speed (mm/s)
1
10
100
1000
10000
I
II
XIV
XIII
XII

FIG. 4

METHOD FOR IMPROVING THE FUEL EFFICIENCY OF ENGINE OIL COMPOSITIONS FOR LARGE LOW AND MEDIUM SPEED GAS ENGINES BY REDUCING THE TRACTION COEFFICIENT

This application claims benefit of U.S. Provisional Application No. 61/337,213 filed Feb. 1, 2010.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to the operation of large engines such as natural gas engines using additized lubricating oil formulations.

2. Description of the Related Art

Natural gas fueled engines are typically four-stroke spark-ignited engines having 12 to 20 cylinders or more similar to heavy duty diesel engines. The engines are typically deployed in the gas and oil industry to compress natural gas at the well heads and along the pipeline. Another common application is distributed power generation or combined heating and power (CHP). Due to the nature of this latter application, the engines fueled by natural gas run continuously near full load conditions, shutting down only for maintenance or oil changes. Higher energy costs result in higher operating costs and create a strong driver for customers to improve the efficiency of their natural gas engine operations. Based on today's natural gas fuel prices, fuel efficiency gains of 1-4% for a typical 1000 bhp gas engine can yield considerable annual savings per engine. In addition, less fuel is burned; proportionately less CO_2 (greenhouse gas) is produced.

Because the lubricant is subjected to a constant high temperature environment, the life of the lubricant is often limited by its oxidation stability. Moreover, because natural gas-fired engines run with high emission of nitrogen oxides (NO_x), the lubricant life may also be limited by its nitration resistance. A longer term requirement is that the lubricant must also maintain cleanliness within the high temperature environment of the engine, especially for critical components such as bearings, cylinder walls, pistons and piston rings. Therefore, it is desirable for gas engine oils to have good cleanliness qualities while promoting long life through enhanced resistance to oxidation and nitration.

Gas engine oil of enhanced life as evidenced by an increase in the resistance of the oil to oxidation, nitration and deposit formation is the subject of U.S. Pat. No. 5,726,133. The gas engine oil of that patent is a low ash gas engine oil comprising a major amount of a base oil of lubricating viscosity and a minor amount of an additive mixture comprising a mixture of detergents comprising at least one alkali or alkaline earth metal salt having a Total Base Number (TBN) of about 250 and less and a second alkali or alkaline earth metal salt having a TBN lower than the aforesaid component. The TBN of this second alkali or alkaline earth metal salt will typically be about half or less that of the first component.

The fully formulated gas engine oil of U.S. Pat. No. 5,726,133 can also typically contain other standard additives known to those skilled in the art, including dispersants (about 0.5 to 8 vol %), phenolic or aminic anti-oxidants (about 0.05 to 1.5 vol %), metal deactivators such as triazoles, alkyl-substituted dimercaptothiadiazoles (about 0.01 to 0.2 vol %), anti-wear additives such as metal dithiophosphates, metal dithiocarbamates, metal xanthates or tricresylphosphates (about 0.05 to 1.5 vol %), pour point depressants such as poly (meth) acrylates or alkyl aromatic polymers (about 0.05-0.6 vol %), anti-foamants such as silicone anti-foaming agents (about 0.005 to 0.15 vol %) and viscosity index improvers, such as olefin copolymers, polymethacrylates, styrene-diene block copolymers, and star copolymers (up to about 15 vol %, preferably up to about 10 vol %).

U.S. Pat. No. 6,191,081 is directed to a lubricating oil composition for natural gas engines comprising a major amount of a base oil of lubricating viscosity and a minor amount of a mixture of one or more metal salicylate detergents and one or more metal phenate and/or metal sulfonate detergents.

The lubricating oil base stock is any natural or synthetic lubricating base oil stock fraction typically having a kinematic viscosity at 100° C. of about 5 to 20 cSt. In a preferred embodiment, the use of a viscosity index improver permits the omission of oil of viscosity about 20 cSt or more at 100° C. from the lube base oil fraction used to make the formulation. Therefore, a preferred base oil is one which contains little, if any, heavy fraction; e.g., little, if any, lube oil fraction of viscosity 20 cSt or higher at 100° C.

The lubricating oil base stock can be derived from natural lubricating oils, synthetic lubricating oils or mixtures thereof. Suitable base stocks include those in API categories I, II and III, where saturates level and Viscosity Index are:

Group I—less than 90% and 80-120, respectively;
Group II—greater than 90% and 80-120, respectively; and
Group III—greater than 90% and greater than 120, respectively.

Suitable lubricating oil base stocks also include base stocks obtained by isomerization of synthetic wax and slack wax, as well as hydrocrackate base stocks produced by hydrocracking (rather than solvent extracting) the aromatic and polar components of the crude.

The mixture of detergents comprises a first metal salt or group of metal salts selected from the group consisting of one or more metal sulfonates(s), salicylate(s), phenate(s) and mixtures thereof having a high TBN of greater than about 150 to 300 or higher, a second metal salt or group of metal salts selected from the group consisting of one or more metal salicylate(s), metal sulfonate(s), metal phenate(s) and mixtures thereof having a medium TBN of greater than about 50 to 150, and a third metal salt or group of metal salts selected from the group consisting of one or more metal sulfonate(s), metal salicylate(s) and mixtures thereof identified as neutral or low TBN, having a TBN of about 10 to 50, the total amount of medium plus neutral/low TBN detergent being about 0.7 vol % or higher (active ingredient) wherein at least one of the medium or low/neutral TBN detergent(s) is metal salicylate, preferably at least one of the medium TBN detergent(s) is a metal salicylate. The total amount of high TBN detergents is about 0.3 vol % or higher (active ingredient). The mixture contains salts of at least two different types, with medium or neutral salicylate being an essential component. The volume ratio (based on active ingredient) of the high TBN detergent to medium plus neutral/low TBN detergent is in the range of about 0.15 to 3.5.

The mixture of detergents is added to the lubricating oil formulation in an amount up to about 10 vol % based on active ingredient in the detergent mixture, preferably in an amount up to about 8 vol % based on active ingredient, more preferably 6 vol % based on active ingredient in the detergent mixture, most preferably between about 1.5 to 5.0 vol %, based on active ingredient in the detergent mixture. Preferably, the total amount of metal salicylate(s) used of all TBNs is in the range of between 0.5 vol % to 4.5 vol %, based on active ingredient of metal salicylate, the combination of the recited metal salts per se or in combination with any additional metal salts or groups of metal salts being used in an amount sufficient to produce a lubricating oil of at least 0.65 wt % sulfated ash content.

U.S. Published Application US2005/0059563 is directed to a lubricating oil composition, automotive gear lubricating composition and fluids useful in the preparation of finished automotive gear lubricants and gear oils comprising a blend of a PAO having a viscosity of between about 40 cSt (mm^2/s) and 1000 cSt (mm^2/s) @ 100° C., and an ester having a viscosity of less than or equal to about 2.0 cSt (mm^2/s) @ 100° C. wherein the blend of PAO and ester has a viscosity index greater than or equal to the viscosity index of the PAO. The composition may further contain thickeners, anti-oxidants, inhibitor packages, anti-rust additives, dispersants, detergents, friction modifiers, traction improving additives, demulsifiers, defoamants, dyes and haze inhibitors.

U.S. Published Application US2003/0191032 is directed to a detergent additive for lubricating oil compositions comprising at least two of low, medium and high TBN detergents, preferably a calcium salicylate. The detergent is in a lubricating oil composition comprising at least one of Group II base stock, Group III base stock or wax isomerate base stock and mixtures thereof, and an optional minor quantity of a co-base stock(s). Co-base stocks include polyalpha olefin oligomeric low and medium and high viscosity oil, di-basic acid esters, polyol esters, other hydrocarbon oils, supplementary hydrocarbyl aromatics and the like.

US Published Application 2006/0276355 is directed to a lubricant blend for enhanced micropitting properties wherein the lubricant comprises at least two base stocks with a viscosity difference between the first and second base stock of greater than 96 cSt (mm^2/s) @ 100° C. At least one base stock is a polyalpha olefin with a viscosity of less than 6 mm^2/s but greater than 2 cSt (mm^2/s), and the second base stock is a synthetic oil with a viscosity greater than 100 cSt (mm^2/s) but less than 300 cSt (mm^2/s) @ 100° C. The second base stock can be a high viscosity polyalpha olefin.

U.S. Published Application 2007/0289897 is directed to a lubricating oil blend comprising at least two base stocks with a viscosity difference between the first and second base stock of greater than 96 cSt (mm^2/s) @ 100° C., the lubricant exhibiting improved air release. The blend contains at least one synthetic PAO having a viscosity of less than 10 cSt (mm^2/s) but greater than 2 cSt (mm^2/s) @ 100° C. and a second synthetic oil having a viscosity greater than 100 cSt (mm^2/s) but less than 300 cSt (mm^2/s) @ 100° C. The lubricant can contain anti-wear, anti-oxidant, defoamant, demulsifier, detergent, dispersant, metal passivator, friction reducer, rust inhibitor additive and mixtures thereof.

U.S. Published Application 2007/0298990 is directed to a lubricating oil comprising at least two base stocks, the first base stock has a viscosity greater than 40 cSt (mm^2/s) @ 100° C. and a molecular weight distribution (MWD) as a function of viscosity at least 10% less than algorithm:

$$MWD=0.2223+1.0232*\log(Kv \text{ at } 100° \text{ C. in cSt})$$

and a second base stock with a viscosity less than 10 cSt (mm^2/s) @ 100° C. Preferably the difference in viscosity between the first and second stocks is greater than 30 cSt (mm^2/s) @ 100° C. Preferably the higher viscosity first stock is a metallocene catalyzed PAO base stock. The second stock can be selected from GTL lubricants, wax-derived lubricants, PAO, brightstock, brightstock with PIB, Group I base stocks, Group II base stocks, Group III base stocks and mixtures thereof. The lubricant can contain additives including detergents. Preferably the first stock has a viscosity of greater than 300 cSt (mm^2/s) @ 100° C., the second stock has a viscosity of between 1.5 cSt (mm^2/s) to 6 cSt (mm^2/s) @ 100° C. Preferably the difference in viscosity between the first and second stocks is greater than 96 cSt (mm^2/s) @ 100° C.

U.S. Published Application US2008/0207475 is directed to a lubricating oil comprising at least two base stocks, the first base stock having a viscosity of at least 300 cSt (mm^2/s) @ 100° C. and a molecular weight distribution (MSD) as a function of viscosity at least 10% less than algorithm:

$$MWD=0.2223+1.0232*\log(KV @ 100° \text{ C. in cSt})$$

and the second stock has a viscosity of less than 100 cSt (mm^2/s) @ 100° C. Preferably the difference in viscosity between the first and second stocks is greater than 250 cSt (mm^2/s) @ 100° C. Preferably the first stock is a metallocene catalyzed PAO base stock. The second stock can be chosen from GTL base stock, wax-derived base stock, PAO, brightstock, brightstock with PIB, Group I base stock, Group II base stock, Group III base stock, Group V base stock, Group VI base stock and mixtures thereof. The lubricant can contain additives including detergents.

U.S. Pat. No. 6,140,281 is directed to long life gas engine lubricating oils containing detergents. The lubricating oil comprises a major amount of a base oil of lubricating viscosity and a minor amount of a mixture of one or more metal sulfonate(s) and/or phenate(s) and one or more metal salicylate(s) detergents, all detergents in the mixture having the same or substantially the same Total Base Number (TBN).

The lubricating oil base stock is any natural or synthetic lubricating base stock fraction typically having a kinematic viscosity at 100° C. of about 5 to 20 cSt (mm^2/s), more preferably about 7 to 16 cSt (mm^2/s), most preferably about 9 to 13 cSt (mm^2/s). In a preferred embodiment, the use of a viscosity index improver permits the omission of oil of viscosity 20 cSt (mm^2/s) or more at 100° C. from the lube base oil fraction used to make the formulation. Therefore, a preferred base oil is one which contains little, if any, heavy fractions; e.g., little, if any, lube oil fraction of viscosity 20 cSt (mm^2/s) or higher at 100° C.

The lubricating oil base stock can be derived from natural lubricating oils, synthetic lubricating oils or mixtures thereof. Suitable base stocks include those in API categories I, II and III, where saturates level and Viscosity Index are:

Group I—less than 90% and 80-120, respectively;
Group II—greater than 90% and 80-120, respectively; and
Group III—greater than 90% and greater than 120, respectively.

Suitable lubricating oil base stocks include base stocks obtained by isomerization of synthetic wax and slack wax, as well as hydrocrackate base stocks produced by hydrocracking (rather than solvent extracting) the aromatic and polar components of the crude.

The detergent is a mixture of one or more metal sulfonate(s) and/or metal phenate(s) with one or more metal salicylate(s). The metals are any alkali or alkaline earth metals; e.g., calcium, barium, sodium, lithium, potassium, magnesium, more preferably calcium, barium and magnesium. It is a feature of the lubricating oil that each of the metal salts used in the mixture.

The TBNs of the salts will differ by no more than about 15%, preferably no more than about 12%, more preferably no more than about 10% or less.

The one or more metal sulfonate(s) and/or metal phenate(s), and the one or more metal salicylate(s) are utilized in the detergent as a mixture, for example, in a ratio by parts of 5:95 to 95:5, preferably 10:90 to 90:10, more preferably 20:80 to 80:20.

The mixture of detergents is added to the lubricating oil formulation in an amount up to about 10 vol % based on active ingredient in the detergent mixture, preferably in an amount up to about 8 vol % based on active ingredient.

U.S. Pat. No. 6,645,922 is directed to a lubricating oil for two-stroke cross-head marine diesel engines comprising a base oil and an oil-soluble overbased detergent additive in the form of a complex wherein the basic material of the detergent is stabilized by more than one surfactant. The more than one surfactants can be mixtures of: (1) sulfurized and/or non-sulfurized phenols and one other surfactant which is not a phenol surfactant; or (2) sulfurized and/or non-sulfurized salicylic acid and one other surfactant which is not a salicylic surfactant; or (3) at least three surfactants which are sulfurized or non-sulfurized phenol, sulfurized or non-sulfurized salicylic acid and one other surfactant which is not a phenol or salicylic surfactant; or (4) at least three surfactants which are sulfurized or non-sulfurized phenol, sulfurized or non-sulfurized salicylic acid and at least one sulfuric acid surfactant.

The base stock is an oil of lubricating viscosity and may be any oil suitable for the system lubrication of a cross-head engine. The lubricating oil may suitably be an animal, vegetable or a mineral oil. Suitably the lubricating oil is a petroleum-derived lubricating oil, such as naphthenic base, paraffinic base or mixed base oil. Alternatively, the lubricating oil may be a synthetic lubricating oil. Suitable synthetic lubricating oils include synthetic ester lubricating oils, which oils include diesters such as di-octyl adipate, di-octyl sebacate and tri-decyl adipate, or polymeric hydrocarbon lubricating oils, for example, liquid polyisobutene and polyalpha olefins. Commonly, a mineral oil is employed. The lubricating oil may generally comprise greater than 60% by mass, typically greater than 70% by mass of the lubricating oil composition and typically have a kinematic viscosity at 100° C. of from 2 to 40 cSt (mm^2/s), for example, from 3 to 15 cSt (mm^2/s), and a viscosity index from 80 to 100, for example, from 90 to 95.

Another class of lubricating oil is hydrocracked oils, where the refining process further breaks down the middle and heavy distillate fractions in the presence of hydrogen at high temperatures and moderate pressures. Hydrocracked oils typically have kinematic viscosity at 100° C. of from 2 to 40 cSt (mm^2/s), for example, from 3 to 15 cSt (mm^2/s), and a viscosity index typically in the range of from 100 to 110, for example, from 105 to 108.

Brightstock refers to base oils which are solvent-extracted, de-asphalted products from vacuum residuum generally having a kinematic viscosity at 100° C. from 28 to 36 cSt (mm^2/s), and are typically used in a proportion of less than 30, preferably less than 20, more preferably less than 15, most preferably less than 10, such as less than 5 mass %, based on the mass of the lubricating oil composition.

U.S. Pat. No. 6,613,724 is directed to gas fueled engine lubricating oils comprising an oil of lubricating viscosity, a detergent including at least one calcium salicylate having a TBN in the range 70 to 245, 0 to 0.2 mass % of nitrogen, based on the mass of the oil composition, of a dispersant and minor amounts of one or more co-additive. The base oil can be any animal, vegetable, mineral oil or synthetic oil. The base oil is used in a proportion of greater than 60 mass % of the composition. The oil typically has a viscosity at 100° C. of from 2 to 40 cSt (mm^2/s), for example 3 to 15 cSt (mm^2/s) and a viscosity index of from 80 to 100. Hydrocracked oils can also be used which have viscosities of 2 to 40 cSt (mm^2/s) at 100° C. and viscosity indices of 100 to 110. Brightstock having a viscosity at 100° C. of from 28 to 36 cSt (mm^2/s) can also be used, typically in a proportion less than 30, preferably less than 20, most preferably less than 5 mass %.

U.S. Pat. No. 7,101,830 is directed to a gas engine oil having a boron content of more than 95 ppm comprising a major amount of a lubricating oil having a viscosity index of 80 to 120, at least 90 mass % saturates, 0.03 mass % or less sulfur and at least one detergent. Metal salicylate is a preferred detergent.

U.S. Pat. No. 4,956,122 is directed to a lubricating oil composition containing a high viscosity synthetic hydrocarbon such as high viscosity PAO, liquid hydrogenated polyisoprenes, or ethylene-alpha olefin copolymers having a viscosity of 40-1000 cSt (mm^2/s) at 100° C., a low viscosity synthetic hydrocarbon having a viscosity of between 1 and 10 cSt (mm^2/s) at 100° C., optionally a low viscosity ester having a viscosity of between 1 and 10 cSt (mm^2/s) at 100° C. and optionally up to 25 wt % of an additive package.

DESCRIPTION OF THE FIGURES

FIG. **1** presents the effect on traction coefficient of different dispersants and/or detergents in lubricating oils containing combinations of base oils, all combinations blended to a base oil viscosity of 9 cSt (mm^2/s) at 100° C., as compared to a mixture of PAO 40/PAO 6 similarly blended to blended oil viscosity of 9 cSt (mm^2/s) at 100° C. but without detergent.

FIG. **2** presents the effect on traction coefficient of different detergents on lubricating oils containing combinations of base oils blended to a base oil viscosity of 9 cSt (mm^2/s) at 100° C. as compared to a mixture of PAO 40/PAO 6 without detergent similarly blended to a viscosity of 9 cSt (mm^2/s) at 100° C.

FIG. **3** shows the effect on traction coefficient of different base stock blends using a combination of phenate and sulfonate detergents.

FIG. **4** shows the effect on traction coefficient of different base stock blends containing a mixture of phenate and sulfonate detergents and in the absence of any other detergents.

DESCRIPTION OF THE INVENTION

The invention is directed to a method for improving the fuel economy of large low and medium speed engines in which the interfacing surface speeds reach at least 3 mm/s This is achieved by reducing the traction coefficient of the engine oil comprising a base oil by using as the base oil a bimodal blend of two different base oils, a first base oil being one or more oils selected from the group consisting of Group III base oils, Group IV base oils, and Group V base oils, which first base oil has a kinematic viscosity at 100° C. of from 2 to 12 cSt (mm^2/s) and a second base oil selected from one or more oils selected from Group IV base oils having a kinematic viscosity at 100° C. of at least 38 cSt (mm^2/s), the difference in kinematic viscosity between the first and second base oils being at least 32 cSt (mm^2/s), the combination of the first and second base oils having a kinematic viscosity at 100° C. of 15 cSt (mm^2/s) or less, and containing 0.5 to 6 wt %, preferably 0.5 to 4 wt %, more preferably 0.5 to 2 wt % (based on active ingredient) of an alkali and/or alkaline earth metal, preferably alkaline earth metal, more preferably calcium, salicylate detergent, or a mixture of alkali and/or alkaline earth metal, preferably alkaline earth metal, more preferably calcium, phenate with alkali and/or alkaline earth metal, preferably alkaline earth metal, more preferably calcium, salicylate, or a mixture of alkali and/or alkaline earth metal, preferably alkaline earth metal, more preferably calcium, phenate and alkali and/or alkaline earth metal, preferably alkaline earth metal, more preferably calcium, sulfonate, wherein the improvement in the fuel economy is evidenced by the engine oil having a traction coefficient which is lower than the traction coefficient of engine oils which are not bimodal or which are not bimodal to the same degree as recited above or which are based on Group I and/or Group II base stocks and which do not contain the aforesaid detergents. As employed herein and in the appended claims the terms "base stock" and "base oil" are used synonymously and interchangeably.

This invention is also directed to a method for improving the fuel economy of large low and medium speed engines that reach surface speeds of at least 3 mm/s, preferably at least 10 mm/s, more preferably at least 30 mm/s, and are lubricated by an engine oil by reducing the traction coefficient of the engine oil used to lubricate the engine, by employing as the engine oil a lubricating oil comprising a first base oil selected from the group consisting of a Group III base oil, Group IV base oil and/or Group V base oil having a kinematic viscosity at 100° C. of from 2 to 12 mm^2/s, and a second base oil selected from Group IV base oils having a kinematic viscosity at 100° C. of at least 38 mm^2/s, the difference in kinematic viscosity between the first and second base oils being at least 32 mm^2/s, the combination of the first and second base oils having a kinematic viscosity at 100° C. of 15 mm^2/s or less, the lubricating oil further containing 0.5 to 6 wt % based on active ingredient of an alkali and/or alkaline earth metal, preferably alkaline earth metal, more preferably calcium, salicylate detergent, or a mixture of alkali and/or alkaline earth metal, preferably alkaline earth metal, more preferably calcium, phenate with alkali and/or alkaline earth metal, preferably alkaline earth metal, more preferably calcium, salicylate, or a mixture of alkali and/or alkaline earth metal, preferably alkaline earth metal, more preferably calcium, phenate and alkali and/or alkaline earth metal, preferably alkaline earth metal, more preferably calcium, sulfonate, wherein the improvement in fuel economy is evidenced by the engine oil having a traction coefficient which is lower than the traction coefficient of an engine oil of the same kinematic viscosity at 100° C. comprising a single base oil component of a Group III base oil, Group IV base oil or Group V base oil or a blend of comparable base oils having a difference in kinematic viscosity between a first and second base oils less than 32 mm^2/s or which are based on Group I and/or Group II base oils, and which do not contain the aforesaid detergents.

Preferably the difference in kinematic viscosity between the first and second base stocks is at least 70 cSt (mm^2/s), more preferably at least 110 cSt (mm^2/s), still more preferably at least 140 cSt (mm^2/s).

The combination of the first and second base stocks preferably has a kinematic viscosity of 7 to 13 cSt (mm^2/s) at 100° C.

Kinematic viscosity is measured by method ASTM D445.

By "surface speed" is meant the velocity at which interfacing surfaces of an engine, e.g. piston and cylinder wall, interfacing bearing surfaces, move past each other when the engine is operating. This surface speed is a primary factor in influencing whether the lubrication regime for the interfacing surfaces is boundary, hydrodynamic or mixed (boundary/hydrodynamic).

The method of the present invention utilizes a bimodal mixture of base stocks. By bimodal in the present specification is meant a mixture of at least two base stocks each having a different kinematic viscosity at 100° C. wherein the difference in kinematic viscosity at 100° C. between the at least two base stocks is at least 32 cSt (mm^2/s). The mixture of the at least two base stocks comprises one or more low kinematic viscosity base stock(s) having a kinematic viscosity at 100° C. of from 2 to 12 cSt (mm^2/s), which base stock is selected from the group consisting of Group III, Group IV and Group V base stocks, preferably Group III and Group IV base stocks, using the API classification in combination with one or more high kinematic viscosity Group IV base stocks having a kinematic viscosity at 100° C. of at least 38 mm^2/s.

Group III base stocks are classified by the American Petroleum Institute as oils containing greater than or equal to 90% saturates, less than or equal to 0.03% sulfur and a viscosity index of greater than or equal to 120. Group III base stocks are usually produced using a three-stage process involving hydrocracking an oil feed stock, such as vacuum gas oil, to remove impurities and to saturate all aromatics which might be present to produce highly paraffinic lube oil stock of very high viscosity index, subjecting the hydrocracked stock to selective catalytic hydrodewaxing which converts normal paraffins into branched paraffins by isomerization followed by hydrofinishing to remove any residual aromatics, sulfur, nitrogen or oxygenates.

The term Group III stocks as used in the present specification and appended claims also embrace non-conventional or unconventional base stocks and/or base oils which include one or a mixture of base stock(s) and/or base oil(s) derived from: (1) one or more Gas-to-Liquids (GTL) materials; as well as (2) hydrodewaxed, or hydroisomerized/cat (and/or solvent) dewaxed base stock(s) and/or base oil(s) derived from synthetic wax, natural wax or waxy feeds, waxy feeds including feeds such as mineral and/or non-mineral oil waxy feed stocks, for example gas oils, slack waxes (derived from the solvent dewaxing of natural oils, mineral oils or synthetic; e.g., Fischer-Tropsch feed stocks) and waxy stocks such as waxy fuels hydrocracker bottoms, waxy raffinate, hydrocrackate, thermal crackates, foots oil or other natural, mineral oil, or even non-petroleum oil derived waxy materials such as waxy materials recovered from coal liquefaction or shale oil, linear or branched hydrocarbyl compounds with carbon number of about 20 or greater, preferably about 30 or greater, and mixtures of such base stocks and/or base oils.

GTL materials are materials that are derived via one or more synthesis, combination, transformation, rearrangement, and/or degradation/deconstructive processes from gaseous carbon-containing compounds, hydrogen-containing compounds and/or elements as feed stocks such as hydrogen, carbon dioxide, carbon monoxide, water, methane, ethane, ethylene, acetylene, propane, propylene, propyne, butane, butylenes and butynes. GTL base stocks and/or base oils are GTL materials of lubricating viscosity that are generally derived from hydrocarbons, for example, waxy synthesized hydrocarbons, that are themselves derived from simpler gaseous carbon-containing compounds, hydrogen-containing compounds and/or elements as feed stocks. GTL base stock(s) and/or base oil(s) include oils boiling in the lube oil boiling range (1) separated/fractionated from synthesized GTL materials such as, for example, by distillation and subsequently subjected to a final wax processing step which involves either or both of a catalytic dewaxing process, or a solvent dewaxing process, to produce lube oils of reduced/low pour point; (2) synthesized wax isomerates, comprising, for example, hydrodewaxed or hydroisomerized cat and/or solvent dewaxed synthesized wax or waxy hydrocarbons; (3) hydrodewaxed or hydroisomerized cat and/or solvent dewaxed Fischer-Tropsch (F-T) material (i.e., hydrocarbons, waxy hydrocarbons, waxes and possible analogous oxygenates); preferably hydrodewaxed or hydroisomerized/followed by cat and/or solvent dewaxing dewaxed F-T waxy hydrocarbons, or hydrodewaxed or hydroisomerized/followed by cat (and/or solvent) dewaxing dewaxed, F-T waxes, or mixtures thereof.

GTL base stock(s) and/or base oil(s) derived from GTL materials, especially, hydrodewaxed or hydroisomerized/followed by cat and/or solvent dewaxed wax or waxy feed, preferably F-T material derived base stock(s) and/or base oil(s), are characterized typically as having kinematic viscosities at 100° C. of from about 2 mm^2/s to about 50 mm^2/s (ASTM D445). For the purposes of the present invention, such GTL base stock(s) and/or base oil(s) employed as the first oil in the bimodal blend are limited to those GTL base stock(s) and/or base oil(s) which have a KV @ 100° C. in the range of from 2 to 12 cSt (mm^2/s). The GTL base stock(s) and/or base oil(s) are further characterized typically as having pour points of −5° C. to about −40° C. or lower (ASTM D97). They are also characterized typically as having viscosity indices of about 80 to about 140 or greater (ASTM D2270).

In addition, the GTL base stock(s) and/or base oil(s) are typically highly paraffinic (>90% saturates), and may contain mixtures of monocycloparaffins and multicycloparaffins in combination with non-cyclic isoparaffins. The ratio of the naphthenic (i.e., cycloparaffin) content in such combinations varies with the catalyst and temperature used. Further, GTL base stock(s) and/or base oil(s) typically have very low sulfur and nitrogen content, generally containing less than about 10 ppm, and more typically less than about 5 ppm of each of these elements. The sulfur and nitrogen content of GTL base stock(s) and/or base oil(s) obtained from F-T material, especially F-T wax, is essentially nil. In addition, the absence of phosphorous and aromatics make this material especially suitable for the formulation of low SAP products.

The term GTL base stock and/or base oil and/or wax isomerate base stock and/or base oil is to be understood as embracing individual fractions of such materials of different viscosity as recovered in the production process, mixtures of two or more of such fractions of similar viscosity, as well as mixtures of one or two or more low viscosity fractions combined with one, two or more higher viscosity fractions to produce a blend wherein the blend exhibits a target kinematic viscosity in the range of 2 to 12 cSt (mm^2/s).

The GTL material, from which the GTL base stock(s) and/or base oil(s) is/are derived is preferably an F-T material (i.e., hydrocarbons, waxy hydrocarbons, wax).

The GTL material from which the GTL base stock(s) and/or base oil(s) is/are derived is an F-T material (i.e., hydrocarbons, waxy hydrocarbons, wax). A slurry F-T synthesis process may be beneficially used for synthesizing the feed from CO and hydrogen and particularly one employing an F-T catalyst comprising a catalytic cobalt component to provide a high Schultz-Flory kinetic alpha for producing the more desirable higher molecular weight paraffins. This process is well known to those skilled in the art.

Useful compositions of GTL base stock(s) and/or base oil(s), hydrodewaxed or hydroisomerized/cat (and/or solvent) dewaxed F-T material derived base stock(s), and wax-derived hydrodewaxed, or hydroisomerized/cat (and/or solvent) dewaxed base stock(s), such as wax isomerates or hydrodewaxates, are recited in U.S. Pat. Nos. 6,080,301; 6,090,989, and 6,165,949, for example.

Base stock(s) and/or base oil(s) derived from waxy feeds, which are also suitable for use as the Group III stocks in this invention, are paraffinic fluids of lubricating viscosity derived from hydrodewaxed, or hydroisomerized/cat (and/or solvent) dewaxed waxy feed stocks of mineral oil, non-mineral oil, non-petroleum, or natural source origin, e.g. feed stocks such as one or more of gas oils, slack wax, waxy fuels hydrocracker bottoms, hydrocarbon raffinates, natural waxes, hydrocrackates, thermal crackates, foots oil, wax from coal liquefaction or from shale oil, or other suitable mineral oil, non-mineral oil, non-petroleum, or natural source derived waxy materials, linear or branched hydrocarbyl compounds with carbon number of about 20 or greater, preferably about 30 or greater, and mixtures of such isomerate/isodewaxate base stock(s) and/or base oil(s).

Slack wax is the wax recovered from any waxy hydrocarbon oil including synthetic oil such as F-T waxy oil or petroleum oils by solvent or auto-refrigerative dewaxing. Solvent dewaxing employs chilled solvent such as methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK), mixtures of MEK/MIBK, mixtures of MEK and toluene, while auto-refrigerative dewaxing employs pressurized, liquefied low boiling hydrocarbons such as propane or butane.

Slack waxes secured from synthetic waxy oils such as F-T waxy oil will usually have zero or nil sulfur and/or nitrogen containing compound content. Slack wax(es) secured from petroleum oils, may contain sulfur and nitrogen-containing compounds. Such heteroatom compounds must be removed by hydrotreating (and not hydrocracking), as for example by hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) so as to avoid subsequent poisoning/deactivation of the hydroisomerization catalyst.

The process of making the lubricant oil base stocks from wax or waxy stocks, e.g. slack wax, F-T wax or waxy feed, may be characterized as an isomerization process. As previously indicated, if slack waxes are used as the feed, they may need to be subjected to a preliminary hydrotreating step under conditions already well known to those skilled in the art to reduce (to levels that would effectively avoid poisoning or deactivating the isomerization catalyst) or to remove sulfur- and nitrogen-containing compounds which would otherwise deactivate the hydroisomerization or hydrodewaxing catalyst used in subsequent steps. If F-T waxes are used, such preliminary treatment is not required because such waxes have only trace amounts (less than about 10 ppm, or more typically less than about 5 ppm to nil each) of sulfur and/or nitrogen compound content. However, some hydrodewaxing catalyst feed F-T waxes may benefit from prehydrotreatment for the removal of oxygenates while others may benefit from oxygenates treatment. The hydroisomerization or hydrodewaxing process may be conducted over a combination of catalysts, or over a single catalyst.

Following any needed hydrodenitrogenation or hydrosulfurization, the hydroprocessing used for the production of base stocks from such waxy feeds may use an amorphous hydrocracking/hydroisomerization catalyst, such as a lube hydrocracking (LHDC) catalysts, for example catalysts containing Co, Mo, Ni, W, Mo, etc., on oxide supports, e.g., alumina, silica, silica/alumina, or a crystalline hydrocracking/hydroisomerization catalyst, preferably a zeolitic catalyst.

Hydrocarbon conversion catalysts useful in the conversion of the n-paraffin waxy feedstocks disclosed herein to form the isoparaffinic hydrocarbon base oil are zeolite catalysts, such as ZSM-5, ZSM-11, ZSM-23, ZSM-35, ZSM-12, ZSM-38, ZSM-48, offretite, ferrierite, zeolite beta, zeolite theta, and zeolite alpha, as disclosed in U.S. Pat. No. 4,906,350. These catalysts are used in combination with Group VIII metals, in particular palladium or platinum. The Group VIII metals may be incorporated into the zeolite catalysts by conventional techniques, such as ion exchange.

Conversion of the waxy feed stock may be conducted over a combination of Pt/zeolite beta and Pt/ZSM-23 catalysts or over such catalysts used in series in the presence of hydrogen. In another embodiment, the process of producing the lubricant oil base stocks comprises hydroisomerization and dewaxing over a single catalyst, such as Pt/ZSM-35. In yet another embodiment, the waxy feed can be fed over a catalyst comprising Group VIII metal loaded ZSM-48, preferably Group VIII noble metal loaded ZSM-48, more preferably Pt/ZSM-48 in either one stage or two stages. In any case, useful hydrocarbon base oil products may be obtained. Catalyst ZSM-48 is described in U.S. Pat. No. 5,075,269.

A dewaxing step, when needed, may be accomplished using one or more of solvent dewaxing, catalytic dewaxing or hydrodewaxing processes or combinations of such processes in any sequence.

In solvent dewaxing, the hydroisomerate may be contacted with chilled solvents such as acetone, methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK), mixtures of ME/MIBK, or mixtures of MEK/toluene and the like, and further chilled to precipitate out the higher pour point material as a waxy solid which is then separated from the solvent-containing lube oil fraction which is the raffinate. The raffinate is typically further chilled in scraped surface chillers to remove more wax solids. Auto-refrigerative dewaxing using low molecular weight hydrocarbons, such as propane, can also be used in which the hydroisomerate is mixed with, e.g., liquid propane, at least a portion of which is flashed off to chill down the hydroisomerate to precipitate out the wax. The wax is separated from the raffinate by filtration, membrane separation or centrifugation. The solvent is then stripped out of the raffinate, which is then fractionated to produce the preferred base stocks useful in the present invention.

In catalytic dewaxing the hydroisomerate is reacted with hydrogen in the presence of a suitable dewaxing catalyst at conditions effective to lower the pour point of the hydroisomerate. Catalytic dewaxing also converts a portion of the hydroisomerate to lower boiling materials which are separated from the heavier base stock fraction. This base stock fraction can then be fractionated into two or more base stocks. Separation of the lower boiling material may be accomplished either prior to or during fractionation of the heavy base stock fraction material into the desired base stocks.

Any dewaxing catalyst which will reduce the pour point of the hydroisomerate and preferably those which provide a large yield of lube oil base stock from the hydroisomerate may be used. These include shape selective molecular sieves which, when combined with at least one catalytic metal component, have been demonstrated as useful for dewaxing petroleum oil fractions and include, for example, ferrierite, mordenite, ZSM-5, ZSM-11, ZSM-23, ZSM-35, ZSM-22 also known as theta one or TON, and the silicoaluminophosphates known as SAPOs. A dewaxing catalyst which has been found to be unexpectedly particularly effective comprises a noble metal, preferably Pt, composited with H-mordenite. The dewaxing may be accomplished with the catalyst in a fixed, fluid or slurry bed. Typical dewaxing conditions include a temperature in the range of from about 400 to 600° F., a pressure of 500 to 900 psig, H_2 treat rate of 1500 to 3500 SCF/B for flow-through reactors and LHSV of 0.1 to 10, preferably 0.2 to 2.0. The dewaxing is typically conducted to convert no more than 40 wt % and preferably no more than 30 wt % of the hydroisomerate having an initial boiling point in the range of 650 to 750° F. to material boiling below its initial boiling point.

The first base stock of the bimodal mixture can also be a Group IV base stock which for the purposes of this specification and the appended claims is identified as polyalpha olefins.

The polyalpha olefins (PAOs) in general are typically comprised of relatively low molecular weight hydrogenated polymers or oligomers of polyalphaolefins which include, but are not limited to, C_2 to about C_{32} alphaolefins, with the C_8 to about C_{16} alphaolefins, such as 1-octene, 1-decene, 1-dodecene and the like, being preferred. The preferred polyalphaolefins are poly-1-octene, poly-1-decene and poly-1-dodecene and mixtures thereof and mixed olefin-derived polyolefins.

The PAO fluids may be conveniently made by the polymerization of one or a mixture of alphaolefins in the presence of a polymerization catalyst such as the Friedel-Crafts catalyst including, for example, aluminum trichloride, boron trifluoride or complexes of boron trifluoride with water, alcohols such as ethanol, propanol or butanol, carboxylic acids or esters such as ethyl acetate or ethyl proprionate. For example, the methods disclosed by U.S. Pat. No. 4,149,178 or U.S. Pat. No. 3,382,291 may be conveniently used herein. Other descriptions of PAO synthesis are found in the following U.S. Pat. Nos. 3,742,082; 3,769,363; 3,876,720; 4,239,930; 4,367,352; 4,413,156; 4,434,408; 4,910,355; 4,956,122; and 5,068,487. The dimers of the C_{14} to C_{18} olefins are described in U.S. Pat. No. 4,218,330.

The PAOs useful in the present invention can also be made by metallocene catalysis. The metallocene-catalyzed PAO (mPAO) can be a copolymer made from at least two or more different alphaolefins, or a homo-polymer made from a single alphaolefin feed employing a metallocene catalyst system.

The metallocene catalyst can be simple metallocenes, substituted metallocenes or bridged metallocene catalysts activated or promoted by, for instance, methylaluminoxane (MAO) or a non-coordinating anion, such as N,N-dimethylanilinium tetrakis(perfluorophenyl)borate or other equivalent non-coordinating anion. mPAO and methods for producing mPAO employing metallocene catalysis are described in WO 2009/123800, WO 2007/011832 and U.S. published application 2009/0036725.

The copolymer mPAO composition is made from at least two alphaolefins of C_3 to C_{30} range and having monomers randomly distributed in the polymers. It is preferred that the average carbon number is at least 4.1. Advantageously, ethylene and propylene, if present in the feed, are present in the amount of less than 50 wt % individually or preferably less than 50 wt % combined. The copolymers can be isotactic, atactic, syndiotactic polymers or any other form of appropriate tacticity.

mPAO can also be made from mixed feed Linear Alpha Olefins (LAOs) comprising at least two and up to 26 different linear alphaolefins selected from C_3 to C_{30} linear alphaolefins. The mixed feed LAO can be obtained, for example, from an ethylene growth processing using an aluminum catalyst or a metallocene catalyst. The growth olefins comprise mostly C_6 to C_{18} LAO. LAOs from other processes can also be used.

The homo-polymer mPAO composition can be made from single alphaolefin chosen from alphaolefins in the C_3 to C_{30} range, preferably C_3 to C_{16}, most preferably C_3 to C_{14} or C_3 to C_{12}. The homo-polymers can be isotactic, atactic, syndiotactic polymers or any other form of appropriate tacticity. The tacticity can be carefully tailored by the polymerization catalyst and polymerization reaction condition chosen or by the hydrogenation condition chosen.

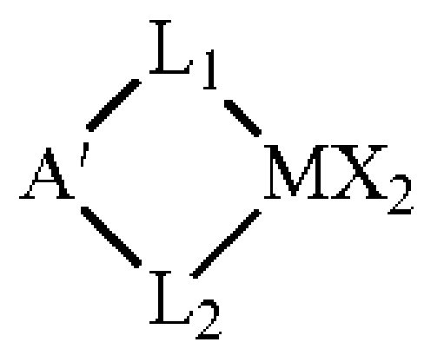
The alphaolefin(s) can be chosen also from any component from a conventional LAO production facility or from a refinery. It can be used alone to make homo-polymer or together with another LAO available from a refinery or chemical plant, including propylene, 1-butene, 1-pentene, and the like, or with 1-hexene or 1-octene made from a dedicated production facility. The alphaolefins also can be chosen from the alphaolefins produced from Fischer-Tropsch synthesis (as reported in U.S. Pat. No. 5,382,739). For example, C_3 to C_{16} alphaolefins, more preferably linear alphaolefins, are suitable to make homo-polymers. Other combinations, such as C_4- and C_{14}-LAO, C_6- and C_{16}-LAO, C_8-, C_{10}-, C_{12}-LAO, or C_8- and C_{14}-LAO, C_6-, C_{10}-, C_{14}-LAO, C_4- and C_{12}-LAO, etc., are suitable to make copolymers.

A feed comprising a mixture of LAOs selected from C_3 to C_{30} LAOs or a single LAO selected from C_3 to C_{16} LAO, is contacted with an activated metallocene catalyst under oligomerization conditions to provide a liquid product suitable for use in lubricant components or as functional fluids. Also embraced are copolymer compositions made from at least two alphaolefins of C_3 to C_{30} range and having monomers randomly distributed in the polymers. The phrase “at least two alphaolefins” will be understood to mean “at least two different alphaolefins” (and similarly “at least three alphaolefins” means “at least three different alphaolefins”, and so forth).

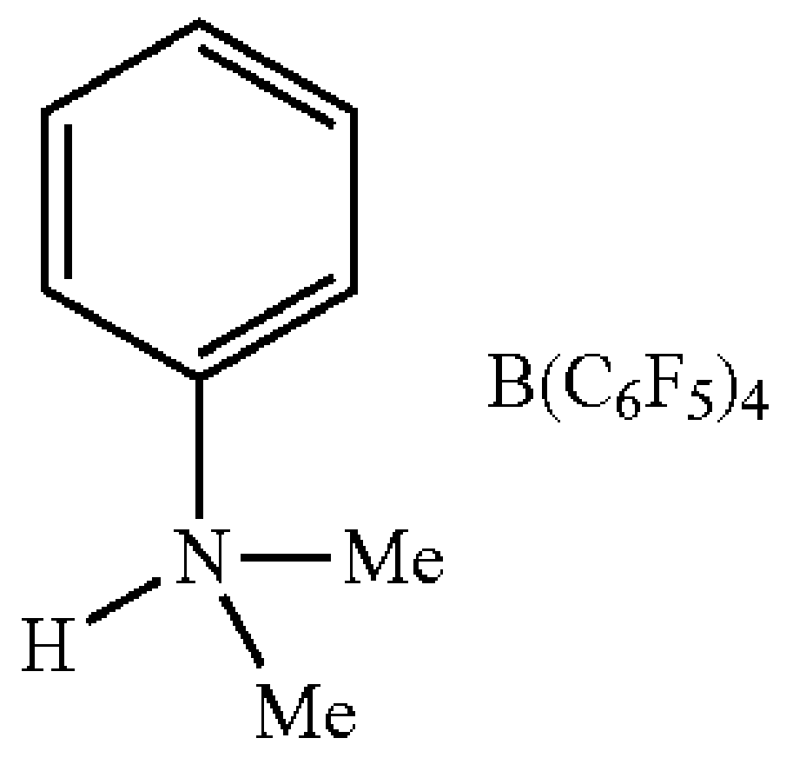
The product obtained is an essentially random liquid copolymer comprising the at least two alphaolefins. By “essentially random” is meant that one of ordinary skill in the art would consider the products to be random copolymer. Likewise the term “liquid” will be understood by one of ordinary skill in the art as meaning liquid under ordinary conditions of temperature and pressure, such as ambient temperature and pressure.

The process for producing mPAO employs a catalyst system comprising a metallocene compound (Formula 1, below) together with an activator such as a non-coordinating anion (NCA) (Formula 2, below) or methylaluminoxane (MAO) 1111 (Formula 3, below):

Formula 1

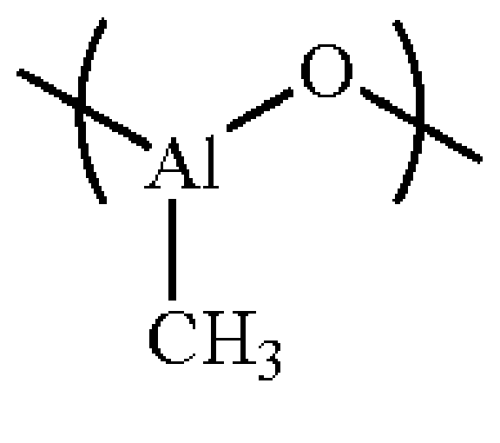


Formula 2



NCA

Formula 3



MAO

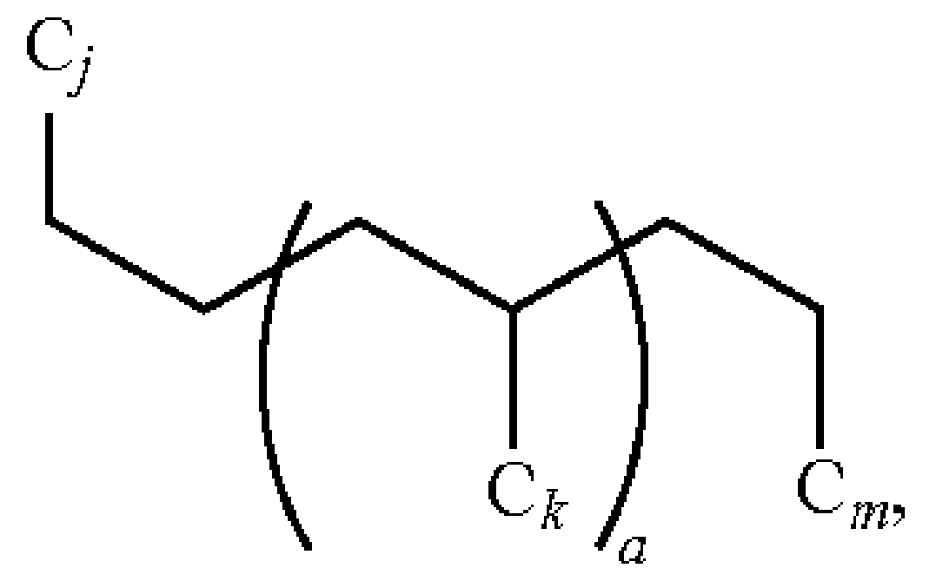
The term “catalyst system” is defined herein to mean a catalyst precursor/activator pair, such as a metallocene/activator pair. When “catalyst system” is used to describe such a pair before activation, it means the unactivated catalyst (precatalyst) together with an activator and, optionally, a co-activator (such as a trialkyl aluminum compound). When it is used to describe such a pair after activation, it means the activated catalyst and the activator or other charge-balancing moiety. Furthermore, this activated “catalyst system” may optionally comprise the co-activator and/or other charge-balancing moiety. Optionally and often, the co-activator, such as trialkyl aluminum compound, is also used as an impurity scavenger.

The metallocene is selected from one or more compounds according to Formula 1 above. In Formula 1, M is selected from Group 4 transition metals, preferably zirconium (Zr), hafnium (Hf) and titanium (Ti), L1 and L2 are independently selected from cyclopentadienyl (“Cp”), indenyl, and fluorenyl, which may be substituted or unsubstituted, and which may be partially hydrogenated. A is an optional bridging group which, if present, can be selected from dialkylsilyl, dialkylmethyl, diphenylsilyl or diphenylmethyl, ethylenyl (—CH_2—CH_2), alkylethylenyl (—CR_2—CR_2), where alkyl can be independently C_1 to C_{16} alkyl radical or phenyl, tolyl, xylyl radical and the like, and wherein each of the two X groups, Xa and Xb, are independently selected from halides OR (R is an alkyl group, preferably selected from C_1 to C_5 straight or branched chain alkyl groups), hydrogen, C_1 to C_{16} alkyl or aryl groups, haloalkyl, and the like. Usually relatively more highly substituted metallocenes give higher catalyst productivity and wider product viscosity ranges.

The polyalphaolefins preferably have a Bromine number of 1.8 or less as measured by ASTM D1159, preferably 1.7 or less, preferably 1.6 or less, preferably 1.5 or less, preferably 1.4 or less, preferably 1.3 or less, preferably 1.2 or less, preferably 1.1 or less, preferably 1.0 or less, preferably 0.5 or less, preferably 0.1 or less. If necessary the polyalphaolefins can be hydrogenated to achieve a low bromine number.

The mpolyalphaolefins (mPAO) described herein may have monomer units represented by Formula 4 in addition to the all regular 1,2-connection:

Formula 4



where j, k and m are each, independently, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21 or 22, n is an integer from 1 to 350 (preferably 1 to 300, preferably 5 to 50) as measured by proton NMR.

Any of the mpolyalphaolefins (mPAO) described herein may have an Mw (weight average molecular weight) of 100,000 or less, preferably between 100 and 80,000, preferably between 250 and 60,000, preferably between 280 and 50,000, preferably between 336 and 40,000 g/mol.

Any of the mpolyalphaolefins (mPAO) described herein may have a Mn (number average molecular weight) of 50,000 or less, preferably between 200 and 40,000, preferably between 250 and 30,000, preferably between 500 and 20,000 g/mol.

Any of the mpolyalphaolefins (mPAO) described herein may have a molecular weight distribution (MWD-Mw/Mn) of greater than 1 and less than 5, preferably less than 4, preferably less than 3, preferably less than 2.5. The MWD of mPAO is always a function of fluid viscosity. Alternately, any of the polyalphaolefins described herein may have an Mw/Mn of between 1 and 2.5, alternately between 1 and 3.5, depending on fluid viscosity.

Molecular weight distribution (MWD), defined as the ratio of weight-averaged MW to number-averaged MW (=Mw/Mn), can be determined by gel permeation chromatography (GPC) using polystyrene standards, as described in p. 115 to 144, Chapter 6, The Molecular Weight of Polymers in “Principles of Polymer Systems” (by Ferdinand Rodrigues, McGraw-Hill Book, 1970). The GPC solvent was HPLC Grade tetrahydrofuran, uninhibited, with a column temperature of 30° C., a flow rate of 1 ml/min, and a sample concentration of 1 wt %, and the Column Set is a Phenogel 500 A, Linear, 10E6A.

Any of the m-polyalphaolefins (mPAO) described herein may have a substantially minor portion of a high end tail of the molecular weight distribution. Preferably, the mPAO has not more than 5.0 wt % of polymer having a molecular weight of greater than 45,000 Daltons. Additionally or alternatively, the amount of the mPAO that has a molecular weight greater than 45,000 Daltons is not more than 1.5 wt %, or not more than 0.10 wt %. Additionally or alternatively, the amount of the mPAO that has a molecular weight greater than 60,000 Daltons is not more than 0.5 wt %, or not more than 0.20 wt %, or not more than 0.1 wt %. The mass fractions at molecular weights of 45,000 and 60,000 can be determined by GPC, as described above.

Any mPAO described herein may have a pour point of less than 0° C. (as measured by ASTM D97), preferably less than −10° C., preferably less than 20° C., preferably less than −25° C., preferably less than −30° C., preferably less than −35° C., preferably less than −50° C., preferably between −10° C. and −80° C., preferably between −15° C. and −70° C.

mPolyalphaolefins (mPAO) made using metallocene catalysis may have a kinematic viscosity at 100° C. from about 1.5 to about 5,000 cSt, preferably from about 2 to about 3,000 cSt, preferably from about 3 cSt to about 1,000 cSt, more preferably from about 4 cSt to about 1,000 cSt, and yet more preferably from about 8 cSt to about 500 cSt as measured by ASTM D445. When used as the first component of the bimodal blend described in the present specification, the mPAO has a KV @ 100° C. in the range 2 to 12 cSt (mm^2/s) while when used as the second component of the bimodal blend the mPAO has a KV @ 100° C. of at least 38 cSt (mm^2/s).

Other PAOs useful as either the first and/or second component in the bimodal blend used in the present invention include those made by the process disclosed in U.S. Pat. Nos. 4,827,064 and 4,827,073. Those PAO materials, which are produced by the use of a reduced valence state chromium catalyst, are olefin oligomers of polymers which are characterized by very high viscosity indices which give them very desirable properties to be useful as lubricant base stocks and, with higher viscosity grades, as VI improvers. They are referred to as High Viscosity Index PAOs or HVI-PAOs.

Various modifications and variations of these HVI-PAO materials are also described in the following U.S. patents to which reference is made: U.S. Pat. Nos. 4,990,709; 5,254,274; 5,132,478; 4,912,272; 5,264,642; 5,243,114; 5,208,403; 5,057,235; 5,104,579; 4,943,383; 4,906,799. These oligomers can be briefly summarized as being produced by the oligomerization of 1-olefins in the presence of a metal oligomerization catalyst which is a supported metal in a reduced valence state. The preferred catalyst comprises a reduced valence state chromium on a silica support, prepared by the reduction of chromium using carbon monoxide as the reducing agent. The oligomerization is carried out at a temperature selected according to the viscosity desired for the resulting oligomer, as described in U.S. Pat. Nos. 4,827,064 and 4,827,073. Higher viscosity materials may be produced as described in U.S. Pat. Nos. 5,012,020 and 5,146,021 where oligomerization temperatures below about 90° C. are used to produce the higher molecular weight oligomers. In all cases, the oligomers, after hydrogenation when necessary to reduce residual unsaturation, have a branching index (as defined in U.S. Pat. Nos. 4,827,064 and 4,827,073) of less than 0.19. Overall, the HVI-PAO normally have a viscosity in the range of about 12 to 5,000 cSt.

Furthermore, the HVI-PAOs generally can be characterized by one or more of the following: C_{30} to C_{1300} hydrocarbons having a branch ratio of less than 0.19, a weight average molecular weight of between 300 and 45,000, a number average molecular weight of between 300 and 18,000, a molecular weight distribution of between 1 and 5. HVI-PAOs are fluids with 100° C. viscosity ranging from 3 to 5000 mm^2/s or more. The fluids with viscosity at 100° C. of 3 mm^2/s to 5000 mm^2/s have VI calculated by ASTM method D2270 greater than 130. Usually they range from 130 to 350. The fluids all have low pour points, below −15° C.

The HVI-PAOs can further be characterized as hydrocarbon compositions comprising the polymers or oligomers made from 1-alkenes, either by itself or in a mixture form, taken from the group consisting of C_6 to C_{20} 1-alkenes. Examples of the feeds can be 1-hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, etc. or mixture of C_6 to C_{14} 1-alkenes or mixture of C_6 to C_{20} 1-alkenes, C_6 and C_{12} 1-alkenes, C_6 and C_{14} 1-alkenes, C_6 and C_{16} 1-alkenes, C_6 and C_{18} 1-alkenes, C_8 and C_{10} 1-alkenes, C_8 and C_{12} 1-alkenes, C_8, C_{10} and C_{12} 1-alkenes, and other appropriate combinations.

The products usually are distilled to remove any low molecular weight compositions such as those boiling below 600° F., or with carbon numbers less than C_{20}, if they are produced from the polymerization reaction or are carried over from the starting material. This distillation step usually improves the volatility of the finished fluids.

The fluids made directly from the polymerization or oligomerization process usually have unsaturated double bonds or have olefinic molecular structure. The amount of double bonds or unsaturation or olefinic components can be measured by several methods, such as bromine number (ASTM D1159), bromine index (ASTM D2710) or other suitable analytical methods, such as NMR, IR, etc. The amount of the double bond or the amount of olefinic compositions depends on several factors—the degree of polymerization, the amount of hydrogen present during the polymerization process and the amount of other promoters which anticipate in the termination steps of the polymerization process, or other agents present in the process. Usually the amount of double bonds or the amount of olefinic components is decreased by the higher degree of polymerization, the higher amount of hydrogen gas present in the polymerization process or the higher amount of promoters participating in the termination steps.

As with the other PAOs, the oxidative stability and light or UV stability of HVI-PAO fluids improves when the amount of unsaturation double bonds or olefinic contents is reduced. Therefore, it is desirable to further hydrotreat the polymer if it has a high degree of unsaturation. Usually the fluids with bromine number of less than 5, as measured by ASTM D1159, is suitable for high quality base stock application. Of course, the lower the bromine number, the better the lube quality. Fluids with bromine numbers of less than 3 or 2 are common. The most preferred range is less than 1 or less than 0.1. The method to hydrotreat to reduce the degree of unsaturation is well known in literature (U.S. Pat. No. 4,827,073, example 16). In some HVI-PAO products, the fluids made directly from the polymerization already have very low degree of unsaturation, such as those with viscosities greater than 150 cSt at 100° C. They have bromine numbers less than 5 or even below 2. In these cases, it can be used as is without hydrotreating, or it can be hydrotreated to further improve the base stock properties.

Regardless of the process or technique used for their production, if the PAO fluid is used as a single component fluid or as one of a mixture of PAO fluids constituting the first low viscosity base stock of the bimodal mixture useful in the present invention, that PAO fluid or blend of PAO fluid is a low kinematic viscosity fluid, a PAO fluid with a KV at 100° C. in the range of 2 to 12 mm^2/s.

The low viscosity fluid can be made up of a single base stock oil meeting the recited kinematic viscosity levels or be made up of two or more base stocks/oils, each meeting the recited kinematic viscosity limits. Further, the low viscosity fluid can be made up of mixtures of one, two or more low viscosity stocks/oils, e.g. stocks/oils with kinematic viscosities in the range of 2 to 12 mm^2/s at 100° C., combined with one, two or more high viscosity stocks/oils, e.g. stocks/oils with kinematic viscosities greater than 12 mm^2/s at 100° C., such as stocks/oils with kinematic viscosities of 100 mm^2/s or greater, provided that the resulting mixture blend exhibits the target low kinematic viscosity of 2 to 12 mm^2/s recited as the viscosity range of the first low viscosity stock.

The second oil used in the bimodal blend is a high kinematic viscosity Group IV fluid, i.e. a PAO with a kinematic viscosity at 100° C. of at least 38 mm^2/s, preferably a kinematic viscosity in the range of about 38 to 1200 mm^2/s, more preferably about 38 to 600 mm^2/s.

In regard to the second, high kinematic viscosity oil, it can be made up of a single PAO base stock/oil meeting the recited kinematic viscosity limit or it may be made up of two or more PAO base stocks/oils, each of which meet the recited kinematic viscosity limit. Conversely, this second, high kinematic viscosity base stock/oil can be a mixture of one, two or more lower kinematic viscosity PAO base stocks/oils, e.g. stocks/oils with kinematic viscosities of less than 38 mm^2/s at 100° C., mixed with one, two or more high kinematic viscosity PAO base stocks/oils, provided that the resulting mixture blend meets the target high kinematic viscosity of at least 38 mm^2/s at 100° C.

Such higher kinematic viscosity PAO fluids can be made using the same PAO synthesis techniques previously recited.

Preferably the high kinematic viscosity PAO fluid which is the second fluid of the bimodal mixture is made employing metallocene catalysis or the process described in U.S. Pat. Nos. 4,827,064 or 4,827,073.

Regardless of the technique or process employed to make PAO, the PAO fluid used as the second base stock of the bimodal blend is a high kinematic viscosity PAO having a KV at 100° C. of at least 38, the only proviso being that the PAO stock used be liquid at ambient temperature.

The present invention achieves its reduction in traction coefficient by use of a lubricant comprising a bimodal blend of two different base oils, the first being one or more Group III and/or Group IV and/or Group V base oils having a KV at 100° C. of from 2 to 12 cSt (mm^2/s) and the second being one or more Group IV base oils having a KV at 100° C. of at least 38 cSt (mm^2/s), provided there is a difference in KV between the first and second base stock of at least 32 cSt (mm^2/s) and the blend has a KV at 100° C. of 15 cSt (mm^2/s) or less. When using such a bimodal blend of base stocks, the traction coefficient of the oil being used at a surface speed of at least about 3 mm/s is reduced as compared to using engine oils which are not bimodal or are bimodal to a lesser degree than as recited or which are based on Group I and/or Group II base stocks and do not contain the recited detergents.

The traction coefficient is reduced at surface speeds as low as about 3 mm/s by using the above recited bimodal base stock blend in combination with a detergent selected from the group consisting of an alkali and/or alkaline earth metal, preferably alkaline earth metal, more preferably calcium, salicylate, a mixture of alkali and/or alkaline earth metal, preferably alkaline earth metal, more preferably calcium, salicylates and alkali and/or alkaline earth metal, preferably alkaline earth metal, more preferably calcium, phenates. The bimodal blend used to reduce traction coefficient at surface speeds of at least 10 mm/s are used in combination with detergents selected from alkali and/or alkaline earth metal, preferably alkaline earth metal, more preferably calcium, salicylates, mixtures of alkali and/or alkaline earth metal, preferably alkaline earth metal, more preferably calcium, salicylates and phenates, and mixtures of alkali and/or alkaline earth metal, preferably alkaline earth metal, more preferably calcium, sulfonates and phenates. At surface speeds of 30 mm/s or higher the bimodal blend used can contain alkali and/or alkaline earth metal, preferably alkaline earth metal, more preferably calcium, phenates as well as any of the aforesaid detergents and detergent pairs. The salts need not be the salt of a single metal but can be a mixture of metal salts, e.g. a mixture of sodium salts and/or lithium salts and/or calcium salts and/or magnesium salts, only by way of example and not limitation.

Depending on the surface speed to be addressed, the engine lubricating oil used to achieve the reduction in traction coefficient comprises as essential components both the bimodal base stock blend and the aforesaid detergents or detergent pairs.

When salicylate detergent or mixtures of salicylate detergent and phenate detergent or mixtures of phenate detergent and sulfonate detergent are employed in the bimodal blend, the detergent(s) is/are present in a total amount in the range 0.5 to 6 wt %, preferably 0.5 to 4 wt %, more preferably 0.5 to 2 wt % of the lubricant (based on detergent active ingredient).

Based on active ingredient, the weight ratio of salicylate to phenate is in the range of 0.75 to 2.0, preferably 1 to 2, and the ratio of sulfonate to phenate is in the range of 0.5 to 1.5, preferably 0.5 to 1.

The detergent(s) used can be of Total Base Number (TBN) in mg KOH/g ranging from neutral/low to high, e.g. TBN 0-40 up to 400 or more, preferably TBN of 0-40 to 300, more preferably TBN of 0-40 to 250.

The finished lubricating oil will have a TBN in the range of 2 to 8, preferably 3 to 7 mg KOH/g.

The amount of detergent(s) used and the TBN of the detergent(s) used will be such that the bimodal lubricant has a sulfated ash content of no more than 1.2 wt %, preferably no more than 0.65 wt %.

The method can use gas engine lubricating oils containing additional performance additives provided the base stock comprises the essential bimodal blend base stock and preferably the bimodal blend base stock and the aforesaid detergents or pairs of detergents, again depending on the surface speed regime to be addressed.

The formulated lubricating oil useful in the present invention may additionally contain one or more of the other commonly used lubricating oil performance additives including but not limited to dispersants, additional other detergents, corrosion inhibitors, rust inhibitors, metal deactivators, other anti-wear and/or extreme pressure additives, anti-seizure agents, wax modifiers, viscosity index improvers, viscosity modifiers, fluid-loss additives, seal compatibility agents, other friction modifiers, lubricity agents, anti-staining agents, chromophoric agents, defoamants, demulsifiers, emulsifiers, densifiers, wetting agents, gelling agents, tackiness agents, colorants, and others. For a review of many commonly used additives, see Klamann in Lubricants and Related Products, Verlag Chemie, Deerfield Beach, Fla.; ISBN 0-89573-177-0. Reference is also made to "Lubricant Additives" by M. W. Ranney, published by Noyes Data Corporation of Parkridge, N.J. (1973).

The types and quantities of performance additives used in combination with the instant invention in lubricant compositions are not limited by the examples shown herein as illustrations.

Viscosity Improvers

Viscosity improvers (also known as Viscosity Index modifiers, and VI improvers) provide lubricants with high and low temperature operability. These additives increase the viscosity of the oil composition at elevated temperatures which increases film thickness, while having limited effect on viscosity at low temperatures.

Suitable viscosity improvers include high molecular weight hydrocarbons, polyesters and viscosity index improver dispersants that function as both a viscosity index improver and a dispersant. Typical molecular weights of these polymers are between about 1,000 to 1,000,000, more typically about 2,000 to 500,000, and even more typically between about 25,000 and 100,000.

Examples of suitable viscosity improvers are polymers and copolymers of methacrylate, butadiene, olefins, or alkylated styrenes. Polyisobutylene is a commonly used viscosity index improver. Another suitable viscosity index improver is polymethacrylate (copolymers of various chain length alkyl methacrylates, for example), some formulations of which also serve as pour point depressants. Other suitable viscosity index improvers include copolymers of ethylene and propylene, hydrogenated block copolymers of styrene and isoprene, and polyacrylates (copolymers of various chain length acrylates, for example). Specific examples include styrene-isoprene or styrene-butadiene based polymers of 50,000 to 200,000 molecular weight.

The amount of viscosity modifier may range from zero to 8 wt %, preferably zero to 4 wt %, more preferably zero to 2 wt % based on active ingredient and depending on the specific viscosity modifier used.

Antioxidants

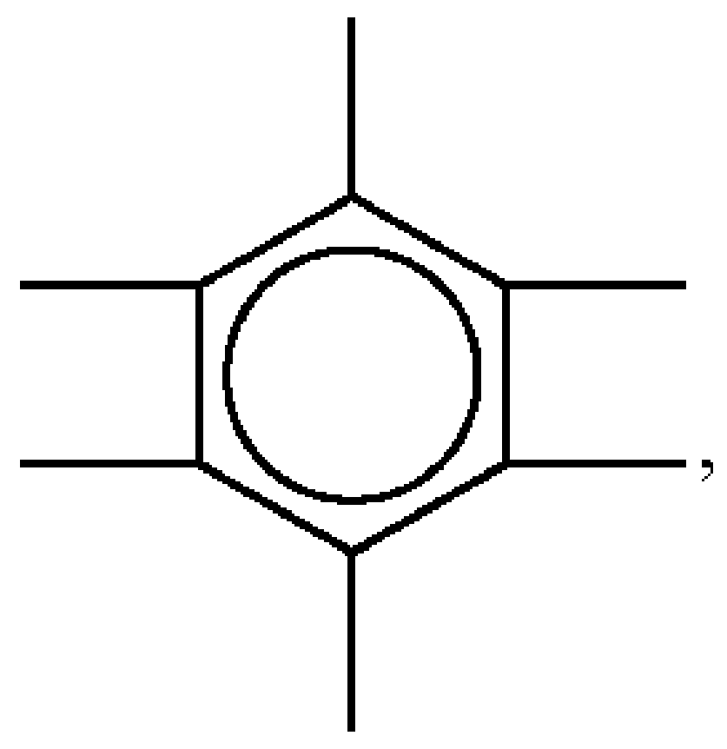
Typical anti-oxidant include phenolic anti-oxidants, aminic anti-oxidants and oil-soluble copper complexes.

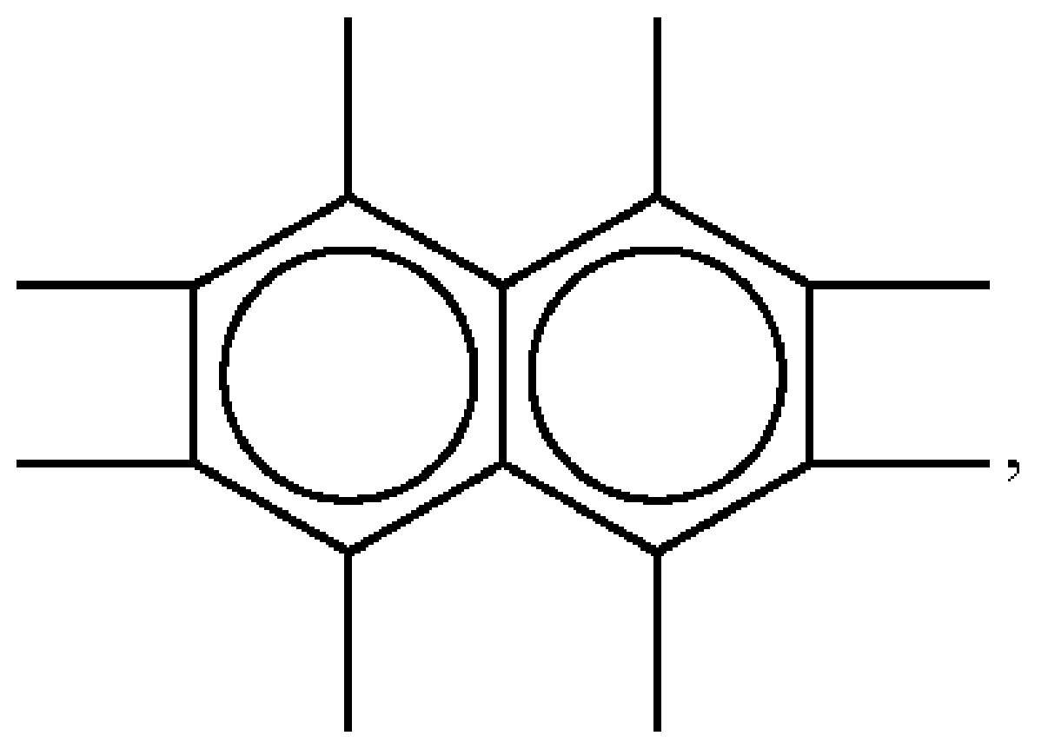
The phenolic anti-oxidants include sulfurized and non-sulfurized phenolic anti-oxidants. The terms "phenolic type" or "phenolic anti-oxidant" used herein includes compounds having one or more than one hydroxyl group bound to an aromatic ring which may itself be mononuclear, e.g., benzyl, or poly-nuclear, e.g., naphthyl and spiro aromatic compounds. Thus "phenol type" includes phenol per se, catechol, resorcinol, hydroquinone, naphthol, etc., as well as alkyl or alkenyl and sulfurized alkyl or alkenyl derivatives thereof, and bisphenol type compounds including such bi-phenol compounds linked by alkylene bridges sulfuric bridges or oxygen bridges. Alkyl phenols include mono- and poly-alkyl or alkenyl phenols, the alkyl or alkenyl group containing from about 3-100 carbons, preferably 4 to 50 carbons and sulfurized derivatives thereof, the number of alkyl or alkenyl groups present in the aromatic ring ranging from 1 to up to the available unsatisfied valences of the aromatic ring remaining after counting the number of hydroxyl groups bound to the aromatic ring.

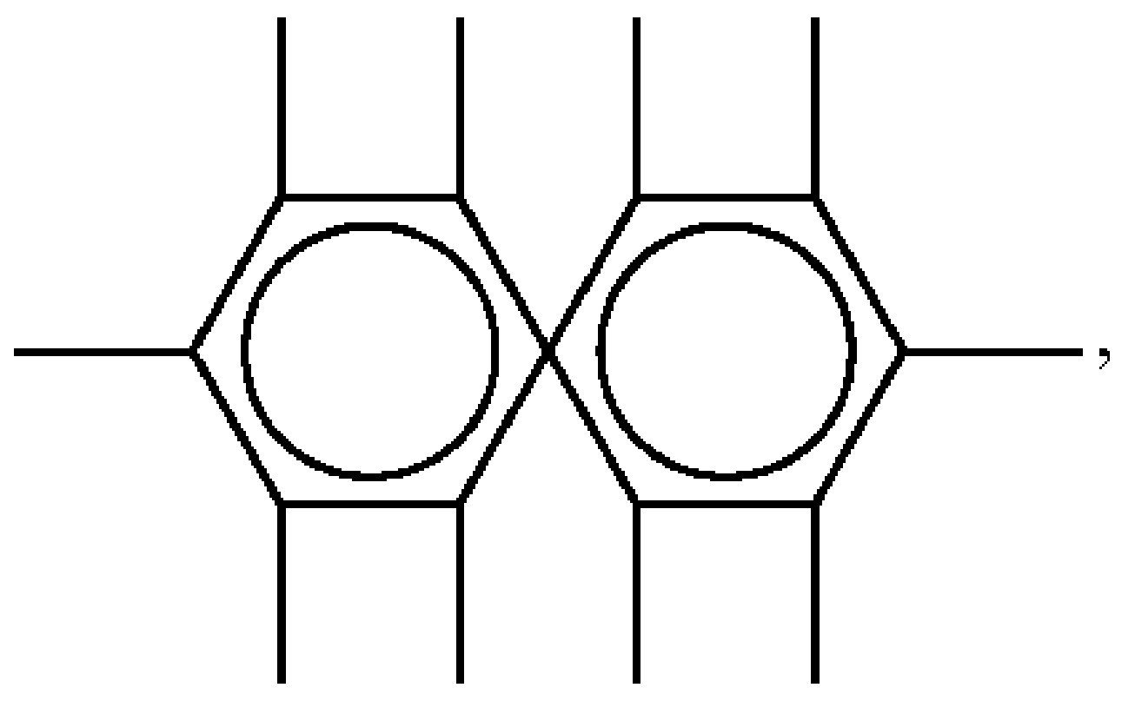
Generally, therefore, the phenolic anti-oxidant may be represented by the general formula:

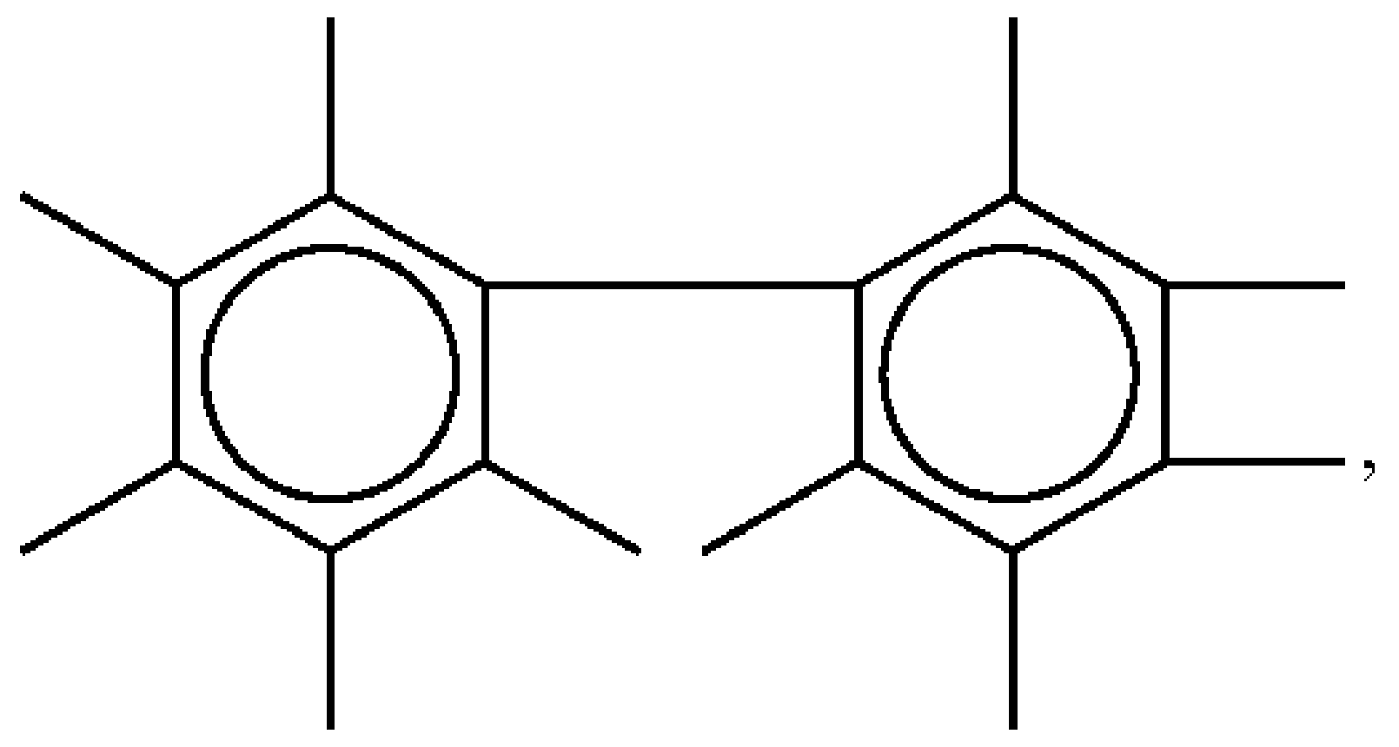
$$(R)_x\text{—Ar—}(OH)_y,$$

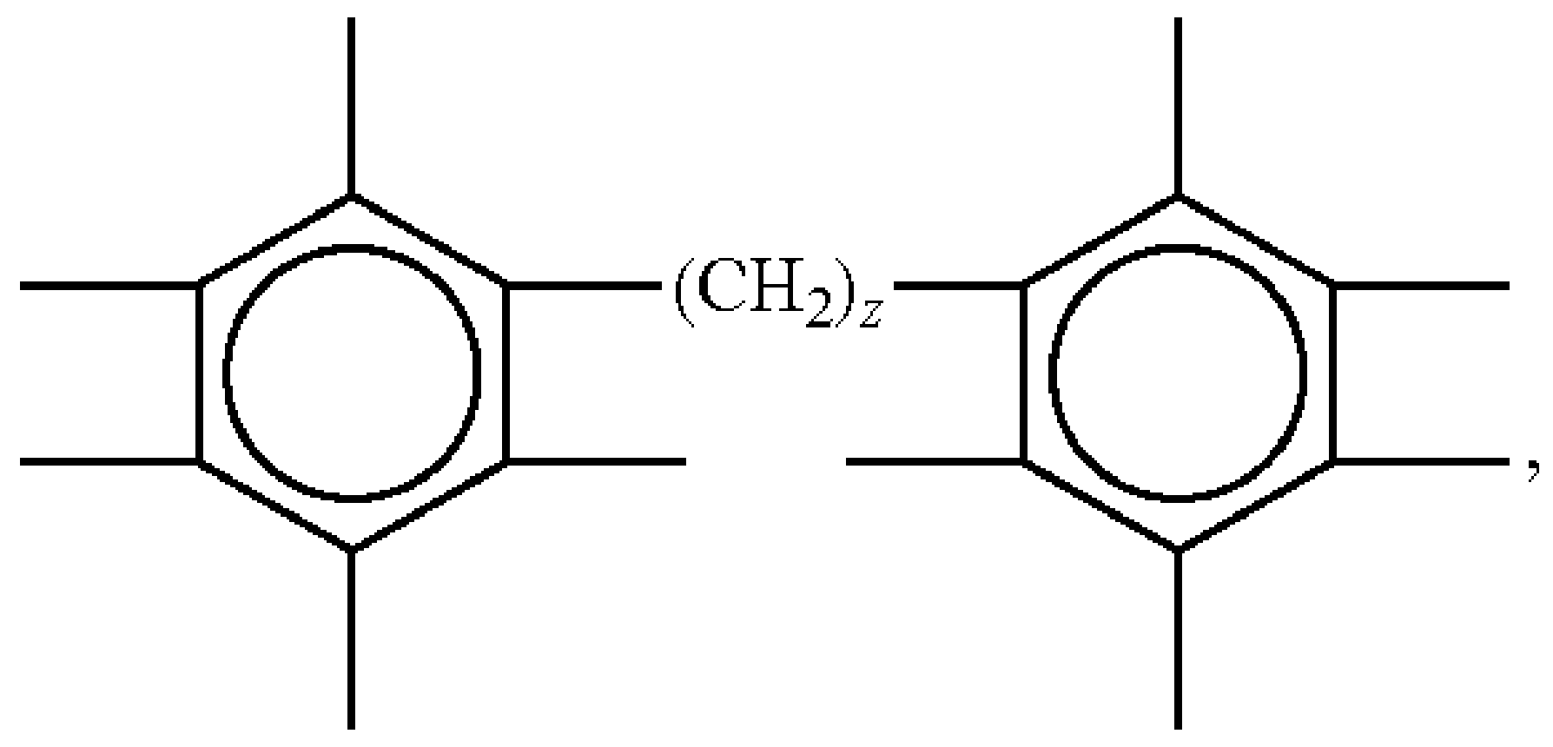
where Ar is selected from the group consisting of:

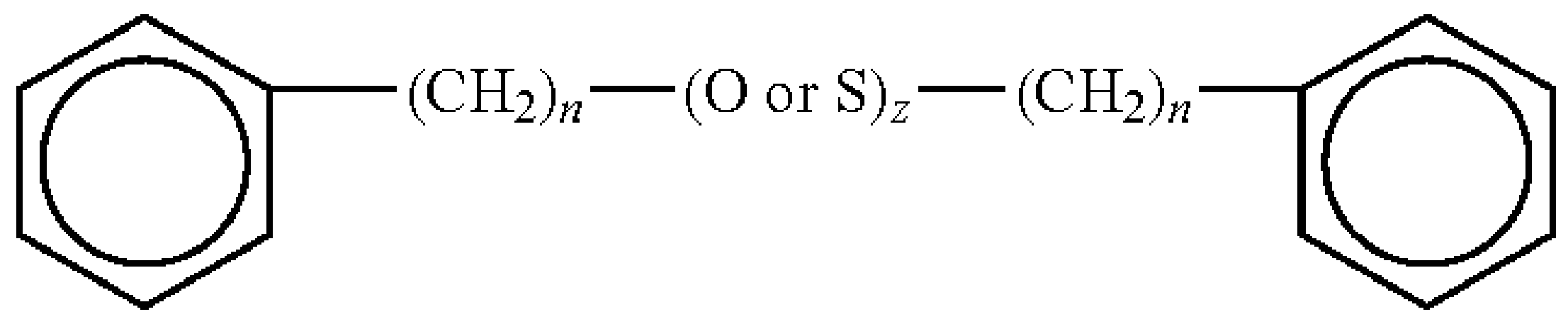


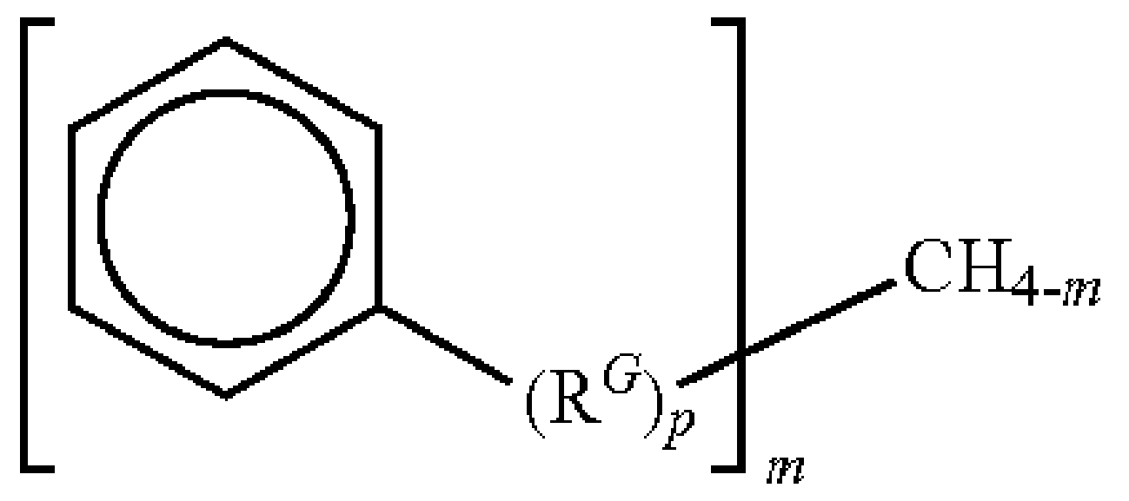










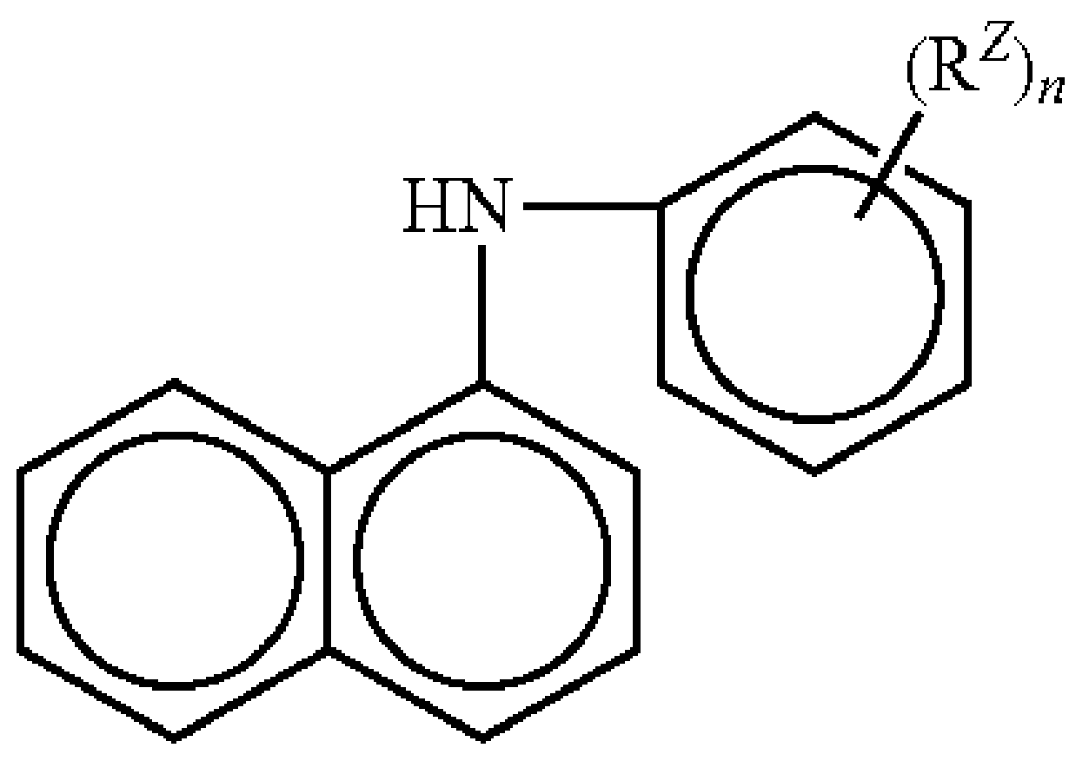


wherein R is a C_3-C_{100} alkyl or alkenyl group, a sulfur substituted alkyl or alkenyl group, preferably a C_4-C_{50} alkyl or alkenyl group or sulfur substituted alkyl or alkenyl group, more preferably C_3-C_{100} alkyl or sulfur substituted alkyl group, most preferably a C_4-C_{50} alkyl group, R^g is a C_1-C_{100} alkylene or sulfur substituted alkylene group, preferably a C_2-C_{50} alkylene or sulfur substituted alkylene group, more preferably a C_2-C_2 alkylene or sulfur substituted alkylene group, y is at least 1 to up to the available valences of Ar, x ranges from 0 to up to the available valances of Ar-y, z ranges from 1 to 10, n ranges from 0 to 20, and m is 0 to 4 and p is 0 or 1, preferably y ranges from 1 to 3, x ranges from 0 to 3, z ranges from 1 to 4 and n ranges from 0 to 5, and p is 0.

Preferred phenolic anti-oxidant compounds are the hindered phenolics which contain a sterically hindered hydroxyl group, and these include those derivatives of dihydroxy aryl compounds in which the hydroxyl groups are in the o- or p-position to each other. Typical phenolic anti-oxidants include the hindered phenols substituted with C_1+ alkyl groups and the alkylene coupled derivatives of these hindered phenols. Examples of phenolic materials of this type 2-t-butyl-4-heptyl phenol; 2-t-butyl-4-octyl phenol; 2-t-butyl-4-dodecyl phenol; 2,6-di-t-butyl-4-heptyl phenol; 2,6-di-t-butyl-4-dodecyl phenol; 2-methyl-6-t-butyl-4-heptyl phenol; 2-methyl-6-t-butyl-4-dodecyl phenol; 2,6-di-t-butyl-4 methyl phenol; 2,6-di-t-butyl-4-ethyl phenol; and 2,6-di-t-butyl 4 alkoxy phenol.

Phenolic type anti-oxidants are well known in the lubricating industry and commercial examples such as Ethanox® 4710, Irganox® 1076, Irganox® L1035, Irganox® 1010, Irganox® L109, Irganox® L118, Irganox® L135 and the like are familiar to those skilled in the art. The above is presented only by way of exemplification, not limitation on the type of phenolic anti-oxidants which can be used.

Aromatic amine anti-oxidants include phenyl-α-naphthyl amine which is described by the following molecular structure:



wherein R^z is hydrogen or a C_1 to C_{14} linear or C_3 to C_{14} branched alkyl group, preferably C_1 to C_{10} linear or C_3 to C_{10} branched alkyl group, more preferably linear or branched C_6 to C_8 and n is an integer ranging from 1 to 5 preferably 1. A particular example is Irganox L06.

Other aromatic amine anti-oxidants include other alkylated and non-alkylated aromatic amines such as aromatic monoamines of the formula $R^8R^9R^{10}N$ where R^8 is an aliphatic, aromatic or substituted aromatic group, R^9 is an aromatic or a substituted aromatic group, and R^{10} is H, alkyl, aryl or $R^{11}S(O)_xR^{12}$ where R^{11} is an alkylene, alkenylene, or aralkylene group, R^{12} is a higher alkyl group, or an alkenyl, aryl, or alkaryl group, and x is 0, 1 or 2. The aliphatic group R^8 may contain from 1 to about 20 carbon atoms, and preferably contains from about 6 to 12 carbon atoms. The aliphatic group is a saturated aliphatic group. Preferably, both R^8 and R^9 are aromatic or substituted aromatic groups, and the aromatic group may be a fused ring aromatic group such as naphthyl. Aromatic groups R^8 and R^9 may be joined together with other groups such as S.

Typical aromatic amines anti-oxidants have alkyl substituent groups of at least about 6 carbon atoms. Examples of aliphatic groups include hexyl, heptyl, octyl, nonyl, and decyl. Generally, the aliphatic groups will not contain more than about 14 carbon atoms. The general types of such other additional amine anti-oxidants which may be present include diphenylamines, phenothiazines, imidodibenzyls and diphenyl phenylene diamines Mixtures of two or more of such other additional aromatic amines may also be present. Polymeric amine anti-oxidants can also be used.

Another class of anti-oxidant used in lubricating oil compositions and which may be present in addition to the necessary phenyl-α-naphthylamine is oil-soluble copper compounds. Any oil-soluble suitable copper compound may be blended into the lubricating oil. Examples of suitable copper anti-oxidants include copper dihydrocarbyl thio- or dithiophosphates and copper salts of carboxylic acid (naturally occurring or synthetic). Other suitable copper salts include copper dithiacarbamates, sulphonates, phenates, and acetylacetonates. Basic, neutral, or acidic copper Cu(I) and or Cu(II) salts derived from alkenyl succinic acids or anhydrides are know to be particularly useful.

Such anti-oxidants may be used in an amount of about 0.50 to 5 wt %, preferably about 0.75 to 3 wt % (on an as-received basis).

Detergents

In addition to the salicylate detergent or detergent pairs previously recited which is/are essential component(s) in the present invention, other detergents known to those skilled in the art may also be present.

Such additional detergents can have total base number (TBN) in mg KOH/g ranging from neutral to highly overbased, i.e. TBN of 0 to over 500, preferably 0-40 to 300, more preferably 0-40 to 250, and they can be present either individually or in combination with each other. Preferably such other detergents are not present in the gas engine oil but, if they are present, they are employed in a minor amount, e.g. less than 50%, of the total detergent mixture, preferably less than 20% of the total detergent mixture, more preferably 10% or less of the total detergent mixture and such that the total amount of all of the detergents present in the formulated lubricating oil is such that the sulfonated ash content of the oil is still no more than 1.2 wt %, preferably no more than 0.65 wt %.

Dispersant

During engine operation, oil-insoluble oxidation byproducts are produced. Dispersants help keep these byproducts in solution, thus diminishing their deposition on metal surfaces. Dispersants may be ashless or ash-forming in nature. Preferably, the dispersant is ashless. So called ashless dispersants are organic materials that form substantially no ash upon combustion. For example, non-metal-containing or borated metal-free dispersants are considered ashless. In contrast, metal-containing detergents discussed above form ash upon combustion.

Suitable dispersants typically contain a polar group attached to a relatively high molecular weight hydrocarbon chain. The polar group typically contains at least one element of nitrogen, oxygen, or phosphorus. Typical hydrocarbon chains contain 50 to 400 carbon atoms.

A particularly useful class of dispersants are the alkenylsuccinic derivatives, typically produced by the reaction of a long chain substituted alkenyl succinic compound, usually a substituted succinic anhydride, with a polyhydroxy or polyamino compound. The long chain group constituting the oleophilic portion of the molecule which confers solubility in the oil, is normally a polyisobutylene group. Many examples of this type of dispersant are well known commercially and in the literature.

Hydrocarbyl-substituted succinic acid compounds are popular dispersants. In particular, succinimide, succinate esters, or succinate ester amides prepared by the reaction of a hydrocarbon-substituted succinic acid compound preferably having at least 50 carbon atoms in the hydrocarbon substituent, with at least one equivalent of an alkylene amine are particularly useful.

Succinimides are formed by the condensation reaction between alkenyl succinic anhydrides and amines. Molar ratios can vary depending on the polyamine. For example, the molar ratio of alkenyl succinic anhydride to TEPA can vary from about 1:1 to about 5:1.

Succinate esters are formed by the condensation reaction between alkenyl succinic anhydrides and alcohols or polyols. Molar ratios can vary depending on the alcohol or polyol used. For example, the condensation product of an alkenyl succinic anhydride and pentaerythritol is a useful dispersant.

Succinate ester amides are formed by condensation reaction between alkenyl succinic anhydrides and alkanol amines For example, suitable alkanol amines include ethoxylated polyalkylpolyamines, propoxylated polyalkylpoly-amines and polyalkenylpolyamines such as polyethylene polyamines One example is propoxylated hexamethylenediamine.

The molecular weight of the alkenyl succinic anhydrides will typically range between 800 and 2,500. The above products can be post-reacted with various reagents such as sulfur, oxygen, formaldehyde, carboxylic acids such as oleic acid, and boron compounds such as borate esters or highly borated dispersants. The dispersants can be borated with from about 0.1 to about 5 moles of boron per mole of dispersant reaction product.

Mannich base dispersants are made from the reaction of alkylphenols, formaldehyde, and amines. Process aids and catalysts, such as oleic acid and sulfonic acids, can also be part of the reaction mixture. Molecular weights of the alkylphenols range from 800 to 2,500.

Typical high molecular weight aliphatic acid modified Mannich condensation products can be prepared from high molecular weight alkyl-substituted hydroxyaromatics or $HN(R)_2$ group-containing reactants.

Examples of high molecular weight alkyl-substituted hydroxyaromatic compounds are polypropylphenol, polybutylphenol, and other polyalkylphenols. These polyalkylphenols can be obtained by the alkylation, in the presence of an alkylating catalyst, such as BF_3, of phenol with high molecular weight polypropylene, polybutylene, and other polyalkylene compounds to give alkyl substituents on the benzene ring of phenol having an average 600-100,000 molecular weight.

Examples of $HN(R)_2$ group-containing reactants are alkylene polyamines, principally polyethylene polyamines. Other representative organic compounds containing at least one $HN(R)_2$ group suitable for use in the preparation of Mannich condensation products are well known and include the mono- and di-amino alkanes and their substituted analogs, e.g., ethylamine and diethanol amine; aromatic diamines, e.g., phenylene diamine, diamino naphthalenes; heterocyclic amines, e.g., morpholine, pyrrole, pyrrolidine, imidazole, imidazolidine, and piperidine; melamine and their substituted analogs.

Examples of alkylene polyamine reactants include ethylenediamine, diethylene triamine, triethylene tetraamine, tetraethylene pentaamine, pentaethylene hexamine, hexaethylene heptaamine, heptaethylene octaamine, octaethylene nonaamine, nonaethylene decamine, and decaethylene undecamine and mixture of such amines having nitrogen contents corresponding to the alkylene polyamines, in the formula $H_2N—(Z—NH—)_nH$, mentioned before, Z is a divalent ethylene and n is 1 to 10 of the foregoing formula. Corresponding propylene polyamines such as propylene diamine and di-, tri-, tetra-, pentapropylene tri-, tetra-, penta- and hexaamines are also suitable reactants. The alkylene polyamines are usually obtained by the reaction of ammonia and dihalo alkanes, such as dichloro alkanes. Thus the alkylene polyamines obtained from the reaction of 2 to 11 moles of ammonia with 1 to 10 moles of dichloroalkanes having 2 to 6 carbon atoms and the chlorines on different carbons are suitable alkylene polyamine reactants.

Aldehyde reactants useful in the preparation of the high molecular products useful in this invention include the aliphatic aldehydes such as formaldehyde (also as paraformaldehyde and formalin), acetaldehyde and aldol (β-hydroxybutyraldehyde). Formaldehyde or a formaldehyde-yielding reactant is preferred.

Preferred dispersants include borated and non-borated succinimides, including those derivatives from mono-succinimides, bis-succinimides, and/or mixtures of mono- and bis-succinimides, wherein the hydrocarbyl succinimide is derived from a hydrocarbylene group such as polyisobutylene having a Mn of from about 500 to about 5000 or a mixture of such hydrocarbylene groups. Other preferred dispersants include succinic acid-esters and amides, alkylphenol-polyamine-coupled Mannich adducts, their capped derivatives, and other related components. Such additives may be used in an amount of about 0.1 to 20 wt %, preferably about 0.1 to 8 wt %, more preferably about 1 to 6 wt % (on an as-received basis) based on the weight of the total lubricant.

Pour Point Depressants

Conventional pour point depressants (also known as lube oil flow improvers) may also be present. Pour point depressant may be added to lower the minimum temperature at which the fluid will flow or can be poured. Examples of suitable pour point depressants include alkylated naphthalenes polymethacrylates, polyacrylates, polyarylamides, condensation products of haloparaffin waxes and aromatic compounds, vinyl carboxylate polymers, and terpolymers of dialkylfumarates, vinyl esters of fatty acids and allyl vinyl ethers.

Such additives may be used in amount of about 0.0 to 0.5 wt %, preferably about 0 to 0.3 wt %, more preferably about 0.001 to 0.1 wt % on an as-received basis.

Corrosion Inhibitors/Metal Deactivators

Corrosion inhibitors are used to reduce the degradation of metallic parts that are in contact with the lubricating oil composition. Suitable corrosion inhibitors include aryl thiazines, alkyl substituted dimercapto thiodiazoles thiadiazoles and mixtures thereof.

Such additives may be used in an amount of about 0.01 to 5 wt %, preferably about 0.01 to 1.5 wt %, more preferably about 0.01 to 0.2 wt %, still more preferably about 0.01 to 0.1 wt % (on an as-received basis) based on the total weight of the lubricating oil composition.

Seal Compatibility Additives

Seal compatibility agents help to swell elastomeric seals by causing a chemical reaction in the fluid or physical change in the elastomer. Suitable seal compatibility agents for lubricating oils include organic phosphates, aromatic esters, aromatic hydrocarbons, esters (butylbenzyl phthalate, for example), and polybutenyl succinic anhydride. Such additives may be used in an amount of about 0.01 to 3 wt %, preferably about 0.01 to 2 wt % on an as-received basis.

Anti-Foam Agents

Anti-foam agents may advantageously be added to lubricant compositions. These agents retard the formation of stable foams. Silicones and organic polymers are typical anti-foam agents. For example, polysiloxanes, such as silicon oil or polydimethyl siloxane, provide antifoam properties. Anti-foam agents are commercially available and may be used in conventional minor amounts along with other additives such as demulsifiers; usually the amount of these additives combined is less than 1 percent, preferably 0.001 to about 0.5 wt %, more preferably about 0.001 to about 0.2 wt %, still more preferably about 0.0001 to 0.15 wt % (on an as-received basis) based on the total weight of the lubricating oil composition.

Inhibitors and Anti-rust Additives

Anti-rust additives (or corrosion inhibitors) are additives that protect lubricated metal surfaces against chemical attack by water or other contaminants. One type of anti-rust additive is a polar compound that wets the metal surface preferentially, protecting it with a film of oil. Another type of anti-rust additive absorbs water by incorporating it in a water-in-oil emulsion so that only the oil touches the surface. Yet another type of anti-rust additive chemically adheres to the metal to produce a non-reactive surface. Examples of suitable additives include zinc dithiophosphates, metal phenolates, basic metal sulfonates, fatty acids and amines. Such additives may be used in an amount of about 0.01 to 5 wt %, preferably about 0.01 to 1.5 wt % on an as-received basis.

Anti-wear additives can also advantageously be present. Anti-wear additives are exemplified by metal dithiophosphate, metal dithiocarbamate, metal dialkyl dithiophosphate, metal xanthage where the metal can be zinc or molybdenum. Tricresylphosphates are another type of anti-wear additive.

Such anti-wear additives can be present in an amount to contribute up to 300 ppm phosphorus in the finished lubricant.

COMPARATIVE EXAMPLES AND EXAMPLES

A series of gas engine oils was evaluated in regard to the effect base stock composition and detergent type has on traction coefficient. The gas engine oils were either a commercially available oil or unadditized base stock or base stock blends or additized base stock or base stock blends. The traction coefficient was measured employing the MTM Traction Rig which is a fully automated Mini Traction Machine traction measurement instrument. The rig is manufactured by PCS Instruments and identified as Model MTM. The test specimens and apparatus configuration are such that realistic pressures, temperatures and speeds can be attained without requiring very large loads, motors or structures. A small sample of fluid (50 ml) is placed in the test cell and the machine automatically runs through a range of speeds, slide-to-roll ratios, temperatures and loads to produce a comprehensive traction map for the test fluid without operational intervention. The standard test specimens are a polished 19.05 mm ball and a 50 0 mm diameter disc manufactured from AISI 52100 bearing steel. The specimens are designed to be single use, throw away items. The ball is loaded against the face of the disc and the ball and disc are driven independently by DC servo motors and drives to allow high precision speed control, particularly at low slide/roll ratios. Each specimen is end mounted on shafts in a small stainless steel test fluid bath. The vertical shaft and drive system which supports the disk test specimen is fixed. However, the shaft and drive system which supports the ball test specimen is supported by a gimbal arrangement such that it can rotate around two orthogonal axes. One axis is normal to the load application direction, the other to the traction force direction. The ball and disk are driven in the same direction. Application of the load and restraint of the traction force is made through high stiffness force transducers appropriately mounted in the gimbal arrangement to minimize the overall support system deflections. The output from these force transducers is monitored directly by a personal computer. The traction coefficient is the ratio of the traction force to the applied load. As shown in FIGS. **1-4**, the traction coefficient was measured over a range of speeds. In FIGS. **1-4**, the speed on the x-axis is the entrainment speed, which is half the sum of the ball and disk speeds. These entrainment speeds simulate the range of surface speeds, or at least a portion of the range of surface speeds, reached when the engine is operating.

The test results presented herein were generated under the following conditions:

Temperature	100° C.
Load	1.0 GPa
Slide-to-roll ratio (SRR)	50%
Speed gradient	0-3000 mm/sec in 480 seconds

The lubricating oils are described in Table 1.

TABLE 1

Oil Designation	Additive System	Base Stock	Base Stock Mixture SAE Grade	Nominal ΔKV @ 100° C. (mm^2/s)	As-Received wt %	TBN	Active Ingredient (AI), wt %	AI Ratio
Reference Oil	Calcium Phenate + Calcium Sulfonate (Pack II)	Group I + Group II	40 (12 mm^2/s)	1-2	2.55	6	1.37	0.5[1]
I	Calcium Phenate + Calcium Salicylate (Pack I)	PAO6 + PAO40	30 (9 mm^2/s)	34	4.5	6	1.95	1.2[2]
II	Calcium Phenate + Calcium Salicylate (Pack I)	PAO6 + PAO150	30 (9 mm^2/s)	144	4.5	6	1.95	1.2[2]
III	Calcium Phenate + Calcium Salicylate (Pack I)	PAO6 + PAO40	20 (6 mm^2/s)	34	4.5	6	1.95	1.2[2]
IV	Calcium Phenate + Calcium Salicylate (Pack I)	PAO6 + PAO150	20 (6 mm^2/s)	144	4.5	6	1.95	1.2[2]
V	NONE	PAO6 + PAO150	30 (9 mm^2/s)	144				
VI	Borated Dispersant (Pack I)	PAO6 + PAO150	30 (9 mm^2/s)	144				
VII	Borated and Non-Borated Dispersant in Pack I	PAO6 + PAO150	30 (9 mm^2/s)	144				
VIII	107-124 TBN Calcium Phenate only (Pack I)	PAO6 + PAO150	30 (9 mm^2/s)	144	1.8	3	0.9	
IX	Non-Borated Dispersant only (Pack I)	PAO6 + PAO150	30 (9 mm^2/s)	144				
X	60-68 TBN Calcium Salicylate only in (Pack I)	PAO6 + PAO150	30 (9 mm^2/s)	144	2.7	3	1.08	
XI	60-68 TBN Calcium Salicylate 107-124 TBN Calcium Phenate (Pack I)	PAO6 + PAO150	30 (9 mm^2/s)	144	4.5	6	1.95	1.2[2]
XII	NONE	PAO6 + PAO40	30 (9 mm^2/s)	34				
XIII	NONE	Group I + Group II	40 (12 mm^2/s)	1-2				

TABLE 1-continued

Oil Designation	Additive System	Base Stock	Base Stock Mixture SAE Grade	Nominal ΔKV @ 100° C. (mm^2/s)	As-Received wt %	TBN	Active Ingredient (AI), wt %	AI Ratio
XIV	Calcium Phenate + Calcium Salicylate (Pack I)	Group I + Group II	40 (12 mm^2/s)	1-2	4.5	6	1.95	1.2[2]
XV	Calcium Phenate + Calcium Sulfonate (Pack II)	PAO6 + PAO40	40 (12 mm^2/s)	34	2.55	6	1.37	0.5[1]

[1] Weight ratio of sulfonate to phenate.

[2] Weightratio of salicylate to phenate.

Additive Pack I nominally contains a mixture of calcium phenate detergent, calcium salicylate detergent, borated dispersant, unborated dispersant, aminic anti-oxidant, phenolic anti-oxidant, ZDDP and metal passivator.

Additive Pack II nominally contains a mixture of calcium phenate, calcium sulfonate, unborated dispersant, aminic anti-oxidant, phenolic anti-oxidant, ZDDP and no metal passivator.

In Table 1 when it is recited, for instance, that the additive complex is calcium phenate and calcium salicylate in Pack I, it means both the phenate and salicylate detergents were present in the additive package system added to the base stock. Conversely when it is recited, for instance, that the additive system is borated dispersant in Pack I, it means that only the borated dispersant is present in Additive Pack I added to the base oil (the normally present unborated dispersant being omitted in that instance). In such a case the amount of the remaining components were not rebalanced to compensate for the missing or omitted component. Further, as used in this specification the designation of a PAO as, for example, PAO 150, means a PAO having a KV at 100° C. of nominally 150 mm^2/s. The PAO 150 used in the examples was made employing metallocene catalysis as previously described. The PAO 40 was made employing aluminum trichloride catalysis as previously described.

These different blends of base stock and blends of base stocks with different additives were compared in various combinations with the results are presented in FIGS. **1**, **2**, **3** and **4**.

FIG. **1** compares different combinations of base oils and combinations of base oils with a variety of different additives and mixtures of additives. The oils compared are Oils X, VI, VII, VIII, IX, XI, XII and Reference Oil.

Oils X, VIII and XI compared oils containing different detergents:

Oil X contained 2.7 wt % (as-received) of 60-68 TBN calcium salicylate.

Oil VIII contained 1.8 wt % (as-received) of 107-124 TBN calcium phenate.

Oil XI employed Pack I which contained 107-124 TBN calcium phenate and 60-68 calcium salicylate at a salicylate: phenate ratio of 1.5 on an as-received basis, a combined treat rate of 4.5 wt % on an as-received basis, and an AI ratio of 1.2.

Oils VI, VII, IX and XII compared oils containing either no additive or different types and mixtures of dispersants.

Oil VI contained 1.7 wt % of a borated dispersant based on active ingredient

Oil VII contained 2.2 wt % of a mixture of borated and unborated dispersant at a ratio of 3:1 as-received or 0.8 based on active ingredient.

Oil IX contained 0.5 wt % unborated dispersant based on active ingredient.

Oil XII contained no additive and was a mixture of PAO6 and PAO40, ΔKV at 100° C. 34 mm^2/s.

As can be seen, the lube oil containing the calcium salicylate or mixture of calcium salicylate and calcium phenate (Oils X and XI) exhibited unexpected superior reduction in traction coefficient at speeds of as low as about 3 mm/s compared against just blends of base oil (Oil XII) and even blends of base oil containing one or more dispersants combined with mixed phenate/sulfonate detergent (Oil VI, VII and IX) or just calcium phenate (Oil VIII).

FIG. **2** presents just the results from comparing Oils VIII, X, XI, XII and Reference Oil, again showing the unexpected results secured from using calcium salicylate or a mixture of calcium salicylate and calcium phenate in a bimodal base stock blend, the result being superior to those achieved using just the bimodal blend base stock by itself or when additized with just calcium phenate.

FIG. **3** shows the unexpected superior results secured when the base stock is a bimodal blend of base stocks having a ΔKV at 100° C. of at least 34 mm^2/s (both with and without detergent additives), Oils XV and XII, compared to oils comprising blends of Group I and Group II base stocks containing the same detergent additives (mixed sulfonate and phenate detergents), Reference Oil and Oil XIII.

Reference Oil is a mixture of Group I and Group II base stocks additized with Pack II which contained a mixture of calcium phenate (itself a 1.6 weight ratio (active ingredient) mixture of 250 TBN and 114 TBN calcium phenate) and 5 TBN calcium sulfonate detergents.

Oil XV is a mixture of PAO6 and PAO40 blended to SAE 40 grade (12 mm^2/s) additized with the same Pack II mixture of calcium phenate and calcium sulfonate as used in the Reference Oil.

Oil XIII is a mixture of just a Group I and a Group II stock.

Oil XII is a mixture of PAO6 and PAO40 blended to SAE grade 30.

As can be seen, the bimodal blend of PAO6 and PAO40, whether additized (Oil XV) with the mixture of phenate and sulfonate detergents or not (Oil XII), exhibited unexpected improvement in traction coefficient down to speeds as low as 10 mm/s compared to Reference Oil and Oil XIII, blends of Group I and Group II base stocks, the improvement becoming even more apparent at higher speeds; e.g. 30 mm/s and 70 mm/s, lining out at about 250 to 500 mm/s

FIG. **4** compares oils of different blends of base stock as such or additized with a mixture of 60 to 68 TBN calcium salicylate and 107 to 124 TBN calcium phenate detergents at a salicylate:phenate ratio of 1.5 on an as-received basis, at a combined treat ratio of 4.5 wt % (as-received) and an active ingredient weight ratio of 1:2 (Pack I).

Oil I is a mixture of PAO6 and PAO40 blended to SAE grade 30 (9 mm^2/s) and containing the Pack I detergent mixture.

Oil II is a mixture of PAO6 and PAO150 blended to SAE grade 30 (9 mm^2/s) and containing the Pack I detergent mixture.

Oil XIV is a mixture of Group I and Group II base stocks blended to SAE grade 40 (12 mm^2/s) and containing the Pack I detergent mixture.

Oil XIII is just a mixture of Group I and Group II base stock blended to SAE grade 40 (12 mm^2/s).

Oil XII is just a mixture of PAO6 and PAO40 blended to SAE grade 30 (9 mm^2/s).

As is seen both the blends of PAO6/PAO40 and PAO6/PAO150 exhibited superior traction coefficient reduction compared to the formulations containing blends of Group I and Group II base stocks (with and without detergents), superior results being achieved at a speed as low as 3 mm/s, becoming more dramatic as speed is increased; i.e. at 10 mm/s, even more pronounced at 30 to 100 mm/s, and lining out at about 250 to 500 mm/s The performance of the detergent additized bimodal blends tracked the performance of Oil XII, which was just the bimodal blend of PAO6/PAO40, at speeds of from about 10 mm/s and higher. As is seen from comparing FIGS. **1**, **2** and **3**, even the performance of Oil VIII, the bimodal blend of PAO6 and PAO150 with just calcium phenate detergent was superior in terms of reduction of traction coefficient over blends of Group I and Group II base stocks, both with and without detergents, at speeds of about 30 mm/s and higher.

What is claimed is:

1. A method for improving the fuel economy of large low and medium speed engines that reach surface speeds of at least 3 mm/s and up to 100 mm/s and are lubricated by an engine oil by reducing the traction coefficient of the engine oil used to lubricate the engine, by employing as the engine oil a lubricating oil comprising a base oil comprising a bimodal blend of two different base oils, a first base oil being one or more oils selected from the group consisting of Group IV base oils, which first base oil has a kinematic viscosity at 100° C. of about 6 mm^2/s, and a second base oil being one or more oils selected from Group IV base oils having a kinematic viscosity at 100° C. of about 150 mm^2/s, the difference in kinematic viscosity between the first and second base oils in the blend being at least 140 mm^2/s, the combination of the first and second base oils having a kinematic viscosity at 100° C. of about 9 mm^2/s or less, the lubricating oil further containing about 1.08 to 1.95 wt % based on active ingredient of a detergent selected from a calcium salicylate or a mixture of calcium phenate and calcium salicylate, wherein the improvement in fuel economy is evidenced by the engine oil having a traction coefficient which is lower than the traction coefficient of engine oils which are not bimodal or which are not bimodal to the same degree as recited or which are based on Group I and/or Group II base oils, and which do not contain the aforesaid detergents.

2. The method of claim **1** wherein the lubricating oil has a sulfated ash content of no more than 1.2 wt %.

3. The method of claim **1** wherein the weight ratio of salicylate detergent to phenate detergent is about 1.2 based on active ingredient.

4. The method of claim **1** wherein the second base oil is a PAO base oil.

5. The method of claim **1** wherein the PAO base oil is made employing metallocene catalysis.

6. The method of claim **1** wherein the PAO base oil is characterized by not more than 5.0 wt % of the polymer having a molecular weight of greater than 45,000 Daltons.

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